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# COAL AS A RECORDER OF INCIPIENT ROCK METAMORPHISM.[1]

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## INTRODUCTION.

ALL geologists are more or less familiar with the results of rock metamorphism, but most of them think of the process as beginning with such obvious changes as extreme induration, development of joints and cleavage planes, and the recrystallization of the mineral content of the rocks. It is probable that many have realized that the features mentioned above are characteristic of advanced stages of metamorphism and that these stages must have been preceded by the formation of less obvious features marking the incipient phases of the same process. These phases, however, have generally been regarded as having no relation to the problems of importance to economic geologists, and consequently they have, until recently, received little attention and no effort has been made to determine the criteria by which they may be recognized and measured.

The object of the present paper is to call attention to the fact that rock metamorphism does not begin with the development of cleavage planes; but all rocks, no matter how recently they may have been deposited, are affected by it; and that the criteria for the determination of the early stages, as well as the sequence of

[1] Presidential address, presented before the Society of Economic Geologists, Charlottesville Meeting, April 28, 1930. Published by permission of the Director of the United States Geological Survey.

these stages, have now been fairly well determined and may readily be used by anyone caring to give the matter attention.

## DEFINITION OF METAMORPHISM.

Before attempting to go further into the subject it is well, perhaps, to consider what rock metamorphism really is. The term metamorphism literally means change of form. If we adhere strictly to the etymology of the term we should not restrict it to any particular change or any kind of rock; but should apply it to all changes that the rocks have undergone. Though etymologically correct, this definition is so broad that, if adhered to, it would completely destroy the scientific value of the term and, therefore, most geologists will probably agree that it should be restricted to important changes that are genetically related; and such changes, the writer understands to be those that are produced by pressure and heat. This interpretation is, therefore, the one on which the present paper is based; but the particular phase of the subject to be considered is the earliest one, or the incipient alteration of sedimentary rocks.

## CONDITIONS ATTENDING INCIPIENT STAGES.

All sediments have necessarily been deposited in water, hence all sedimentary rocks consisted originally of an appreciable percentage of water, either in combination with other chemical compounds, or as interstitial water filling voids in the deposited material. As soon as deposition occurred, the material was subjected to the pressure of its own weight and later to that was added the weight of superincumbent beds. At first this may have been so small as to be negligible but, as time elapsed, and more and more material accumulated in the basin of deposition, the pressure increased. The change produced in a few years by the mere weight of the overlying load may not have been very great but, if the pressure were continued for an indefinite length of time, it may have been sufficient to produce very decided changes in the materials deposited—such as sand, gravel, clay, and the remains of plants and animals. In the same manner we must recognize that

the interior heat of the earth, though seemingly infinitesimal in amount and intensity, as observed at the surface, will in the course of time—and Nature has ever been lavish of time—produce very important changes in many of these substances.

This may seem like quibbling over things of slight importance but, while it is perfectly obvious that pressure and heat developed near the surface of the earth by the mere weight of deposited material produce results that are slight in comparison with the results of stresses that have folded the rocks of large areas,—such, for example, as the Appalachian region—they are always present and doubtless have produced, when in action for long periods of time, very perceptible results. In man-made laboratories such slight activities show very small or no results, but in Nature's laboratory no activity is too slight to be disregarded, and a slight pressure exerted for a very long period of time may be even more effective than a much greater pressure exerted for only a short time. It frequently happens that our progress in science is marked by our readiness to consider slight activities as the means by which great results have been accomplished, rather than by cataclysmic action which was appealed to so extensively in the early days of geologic research.

### MATERIALS WHICH RECORD SLIGHT METAMORPHIC ACTION.

The materials which are most readily affected by earth pressures and which are of common occurrence, are the hydrocarbon compounds. These are usually found in their native condition as petroleum or coal in some of the various forms assumed by these substances.

Petroleum at once suggests itself as a compound that is more susceptible to changes of temperature and pressure than any other, and many geologists have attempted to trace the stages of incipient metamorphism by the different petroleum products found in the rocks. This line of approach has not been entirely successful because of the volatile nature of the materials which, with slight changes in metamorphic action, have left little or no residue to mark the progressive stages through which they have passed.

Coupled with this lack of an intelligible record of events is the fact that little is positively known regarding the composition and condition of the material from which petroleum was derived. On the whole, as understood today, petroleum and its products do not afford a complete and reliable record of the varied geologic conditions through which they have passed and consequently they are of little value in determining and establishing the various stages of incipient metamorphism.

Coal is a much more promising material. It is almost universally recognized as having originated from vegetal material and consequently is readily affected by pressure and heat. It also has a decided advantage over petroleum in that it is not destroyed by the agents of metamorphism, unless they have reached a stage of extreme intensity, and consequently under ordinary conditions it leaves residual material to mark the latest stage through which it has passed.

Geologists are not in agreement regarding the interpretation of these residual products. In foreign countries there is a common belief that variations in coal are due to differences in the original vegetal material, but in this country it is generally understood that all coals, though differing somewhat in the materials from which they were derived, are passing through a common historical sequence of events and that the differences that we see today are primarily due to the stage which the coals have reached in this sequence.

This explanation has been gradually evolved as more and more data have been secured regarding the distribution of the different kinds of coal; their relation to areas of great geological disturbance; and the chemical composition of the coals themselves. Henry D. Rogers, State Geologist of Pennsylvania, caught a glimpse of this relationship when in 1858 he discovered that the coals in his State gradually increased in value toward the southeast, but he did not understand the reason for this change. Because of this lack of understanding, he did not realize that the history of the development of coals could be written only when a fairly complete sequence had been studied,—a sequence that should

include the beginning of the transformation as well as its end product.

For a long time after the pioneer work of Rogers, little attention was given in this country to the study of coal and that which was carried on was limited to the high-rank [2] coals mined in the eastern states. Vague descriptions of younger coals in the Far West had been given by private explorers and by Government geologists, but these were of little value, because they were not founded on a thorough study of the material in question and were without reliable chemical analyses to show the composition of the coal. Complete knowledge of these younger coals was not possible until after the year 1905, following the work of the Government coal-testing laboratory at the St. Louis Exposition, when the systematic examination of the western coal fields was begun. The special object of this work was the appraisal by the U. S. Geological Survey of the coal land remaining in the Public Domain, and it has been carried on systematically from that date down to the present time.

The results of this work have afforded definite knowledge of the character and distribution of the various ranks of coal in the West and their geographical relation to areas in which the rocks have suffered severe geologic deformation. Coupled with this were the studies of White, Thiessen, and Davis on the origin of coal and more recently the publication by White [3] of a discussion of the factors involved in the transformation of vegetal matter into various kinds of coal through rock metamorphism. As a result of these studies our knowledge of the character, distribution, and development of coal in general has been so increased that now it seems possible to state with considerable certainty the manner in which coal was formed and how the original material has subsequently been modified by pressure and heat.

[2] The term rank is now generally employed to designate the degree of development of coal.

[3] "The Origin of Coal," U. S. Bureau of Mines, Bull. 38, 1913, and "Some Factors in Rock Metamorphism," by David White, *Proc. Nat. Acad. Sci.*, vol. 14, pp. 5–7, 1928.

## QUALITY OF COAL RELATED TO GEOLOGIC STRUCTURE.

In a close study of the distribution of coal it was found that almost every field shows a close agreement between the distribution of the different kinds of coal contained therein and the deformation of the rocks. If such an agreement were found in one field only, it might be regarded as fortuitous, but when it is found to be characteristic of almost every field that has been studied, it can no longer be referred to that class; and the features in common in the various fields must be regarded as related effects of some general cause. In order to make this clear the writer will describe some of the most striking cases of agreement between rank of coal and intensity of compression due to loading or to lateral thrusts.

In making comparison of the quality of coal it is desirable that the samples should be taken from the same coal bed if possible, because when this is done it lessens the possibility of variations due to different conditions of growth of the original vegetation and also to different conditions of sedimentation. Fortunately in the northern part of the Appalachian coal field it is possible to compare samples of the Pittsburgh coal bed, taken from large mines, on an almost continuous line of outcrop, 130 miles in length and extending at right angles to the major axis of the trough containing the coal-bearing rocks. This cross-section, represented by Fig. 1, begins at a point in Ohio about 25 miles west of Wheeling, W. Va., and continues southeastward to the vicinity of Cumberland, Md., at the extreme edge of the coal field.

At the westermost point in Ohio, as shown at *A* on the section, the Pittsburgh coal has a fixed carbon content of 43.8 per cent. In passing eastward this increases to 48.3 per cent. at (*B*) Wheeling, W. Va.; 55.9 per cent. at (*C*) West Brownsville, Pa.; 58.2 per cent. at (*D*) Fairchance, Pa., in the Connellsville coking basin; 67.8 per cent. at (*E*) Meyersdale, Pa.; and 73.2 per cent. at (*F*) Frostburg, Md., a few miles west of Cumberland. Conversely, the volatile matter decreases steadily from 42.7 per cent. in Ohio to 17.9 per cent. at Frostburg. As the blocks in the diagram,

representing the chemical composition of the coal, are correctly spaced with reference to the section as a whole, it will be seen that the line drawn at the top of the fixed carbon content ascends with remarkable regularity from one end of the section to the

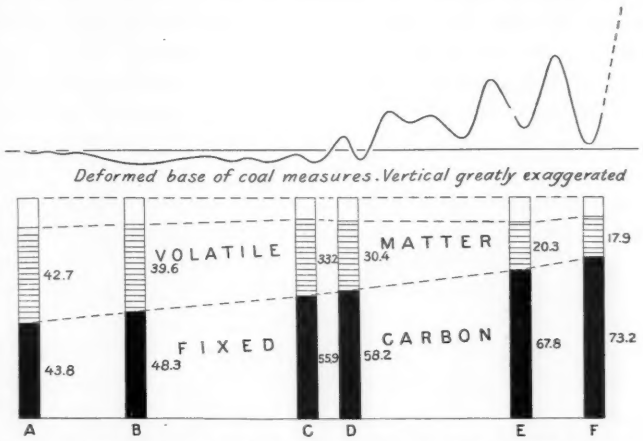


FIG. 1. Diagrams showing the composition of the Pittsburgh coal along a line extending from Ohio to near Cumberland, Md. *A*, a mine 25 mi. west of Wheeling, W. V.; *B*, Wheeling, W. Va.; *C*, West Brownsville, Pa.; *D*, Fairchance, Pa.; *E*, Meyersdale, Pa.; and *F*, Frostburg, near Cumberland, Md.

other, showing that the chemical composition of the coal changes gradually and steadily along this line for a distance of 130 miles.

Not only does the chemical composition change in this distance, but there is also a marked change in the physical properties of the coal. In Ohio the Pittsburgh coal is hard and distinctly laminated. In mining it breaks out in large blocks bounded by joint planes but splits readily along the bedding planes. In an eastward direction these physical characteristics change; joint or cleavage planes are more and more highly developed, until at Frostburg the coal is cut so closely by them that it appears to be composed of an infinite number of minute prisms, standing generally at right

angles to the bedding planes, and it is so friable that one can crush a lump of considerable size in his hand.

It is evident therefore that in passing from Ohio to Cumberland, Md., the Pittsburgh coal has suffered a very decided change not only in its chemical composition but also in its physical properties, and that these changes coincide with an increase in the quality of the coal or, in other words, in its rank.

Let us now examine the geologic side of the problem and see if this decided change in the coal is in any way related to geologic conditions. It is well known that the rocks in the coal field of eastern Ohio are nearly horizontal, dipping only slightly into the great basin whose axis is located a short distance east of Ohio River, and they have suffered little metamorphism, but in the vicinity of Cumberland they are thrown into great folds which involve tens of thousands of feet of rocky strata. In order to visualize this change, there is added to the diagram a line representing the deformed surface of the base of the coal-bearing rocks, with the vertical element greatly exaggerated so that all the major folds may be seen. From this line it is evident that the rocks in Ohio are practically flat, and that this condition holds across Ohio River at Wheeling. East of Wheeling small folds appear, but it is not until Fairchance is passed that the folds become prominent, both in the section and also in the field. The folds increase in magnitude eastward until at Cumberland they are too large to be shown in the diagram. There are some apparent irregularities and lack of agreement in detail between the geologic section and the percentage of fixed carbon but time will not permit of a discussion of this subject, except to say that a critical study of the conditions leads the writer to believe that the irregularities are in reality slight in comparison with the points of agreement and that all can be explained on the theory that the rocks are not homogeneous and consequently that stresses are irregular and have produced more decided results in some localities than they have in others.

The next example of change in coal due to pressure is of a different order. It is introduced to show the effect of very slight

stresses which have not been sufficient to change materially the volatile matter and the fixed carbon, but have been adequate to reduce the percentage of moisture to a considerable extent. The area in question is known to geologists as the Ozark Dome in southern Missouri and northern Arkansas and the surrounding coal fields of Oklahoma, Kansas, Missouri, Iowa, Illinois, Indiana, and western Kentucky, as shown in Fig. 2.

FIG. 2. Map of coal fields surrounding the Ozark Dome, showing by lines of equal moisture content the effect of the domal uplift.

The effect of stresses produced by the upthrusting of this dome are best shown by lines connecting points at which the coal has the same percentage of moisture. In practically all cases the moisture content increases as distance is gained from the dome. Thus the line connecting points at which the coal has a moisture content of 5 per cent. is shown by the first or southermost line

that extends from the southern part of Oklahoma rudely parallel with the boundary of the coal-bearing rocks to a point in Missouri about 50 miles east of the Kansas line. It can not be followed continuously eastward because of the lack of coal-bearing rocks, but it reappears in the extreme southern part of Illinois and in Kentucky.

The line connecting points having a moisture content of 10 per cent. lies about 35 miles farther from the dome and can be traced from the city of Tulsa, Oklahoma, northeastward through Fort Scott, Kansas, to a point a little north of Jefferson City, Missouri. At the last-named point the line passes out of the coal field, but, if it were extended rudely parallel with the 5 per cent. line it would coincide with points just south of St. Louis, at which the coal has about the same moisture content.

Similarly the line representing a moisture content of 12 per cent. parallels the line just described across Kansas at a distance of about 40 miles. East of Kansas City, however, it swings to the north in a pronounced loop, as far as Chillicothe and then returns to about the normal distance from the line marking a moisture content of 10 per cent. The line connecting points having a moisture content of 15 per cent. is somewhat more erratic than the line just described, as it apparently swings north as far as Osceola, Iowa, and thence returns with a sharp bend to its normal position in the eastern part of Missouri and thence into Illinois. The line of 20 per cent. moisture rudely parallels the 15 per cent. line in its swing across the northwestern corner of Missouri and thence northward to Fort Dodge, Iowa. This line is not continued eastward because there is no known coal in either eastern Iowa or northern Illinois with so high a moisture content as 20 per cent.

All the lines are quite irregular in Illinois and Kentucky because the effect of the Ozark uplift is complicated and to a certain extent nullified by local disturbances in the rocks, such as the La Salle and other anticlines in Illinois and similar disturbances in western Kentucky. In the area west of Mississippi River, however, there is remarkable parallelism in the lines of equal moisture,

except in the loop to the north near the middle of Missouri and Iowa. When these lines are compared with the structure sections shown in plates 1, 2, and 3, vol. 13, 2d ser. Mo. Geol. Survey, 1915, "The Stratigraphy of the Pennsylvania series in Missouri," it will be seen that in a rude way the northward projection corresponds with minor elevations or anticlines in the structure and therefore, tends rather to confirm the proposition that the writer is putting forward than to detract from it.

In addition to the cases showing agreement between the composition of the coal and the degree of deformation of the associated rocks in the eastern part of the United States, it is well to consider conditions in the Rocky Mountain region where crustal movements have taken place more recently than they have in the East and where their effect is more easily seen. In the mountains the coal fields occupy residual structural basins left, as such, when the adjacent mountains were uplifted. In practically every case the coal in a basin increases in rank toward the margin of the field next to the mountains and is greatest in the rim that is upturned against the mountain flank. In the basins there is not only a decrease in the moisture content of the coal toward the mountains, but also a decided change in the relative proportion of fixed carbon and volatile matter.

One of the most striking cases is that of the great San Juan structural basin in northwestern New Mexico and southwestern Colorado which is represented by Fig. 3. The Cretaceous coal beds underlie, as far as known, this entire basin and on the southern margin at Gallup on the Santa Fe Railroad the coal is a rather high-rank sub-bituminous coal, as shown by the rapidity with which it slacks when exposed to the weather, its high moisture content, and its low heating value. At the north end of the basin where the coal-bearing rocks are upturned against the San Juan Mountains and on the east side where they are similarly situated with regard to the Sierra Naciemento the coal is of bituminous rank and has been successfully manufactured into coke. This shows conclusively that the mountainous uplifts have been responsible for the alteration of the coal and that the metamor-

phosing effects of these crustal disturbances die out as distance is gained away from the mountains.

Examples of the effect of rock deformation on the coals of this region could be multiplied indefinitely, but enough has been

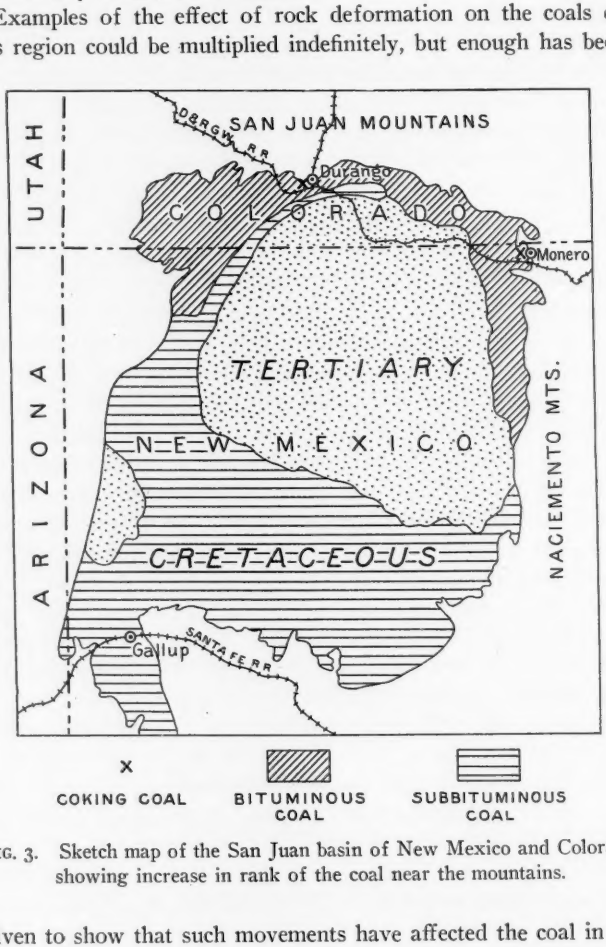


FIG. 3. Sketch map of the San Juan basin of New Mexico and Colorado, showing increase in rank of the coal near the mountains.

given to show that such movements have affected the coal in the West as well as in the East; in other words the stresses which caused rock deformation produced similar results wherever they

have been active and the most pronounced change is found in the coal beds that have been most affected by the movements.

The next phase of the question to be considered is that of the possible recognition of particular stages in the process of regional metamorphism of the coal and the relation of these stages to those that have left their effects on the associated rocks. In considering this phase of the subject it is necessary first to understand clearly the nature of the material from which coal was derived, and second the physical conditions under which it developed into the bedded deposit we know as coal.

### STAGES OF INCIPIENT METAMORPHISM.

*Original Material.*—The theory generally held in this country regarding the formation of coal is that originally it was a swamp growth of vegetation which naturally changed with the geologic periods, ranging from calamites, lepidodendron, and tree-ferns, in the Carboniferous to deciduous trees of essentially the same genera that we have today in the coals of the Eocene and Miocene epochs of the Tertiary. This idea of the origin is not accepted generally abroad, where it is supposed that the plants grew on land, but later were washed into the sea and there were entombed and converted into coal. It is not necessary here to go into this subject in detail, but it is desirable to understand that there is a difference of opinion on this subject. American geologists feel that they have ample evidence to prove the correctness of their conclusions, so the swamp hypothesis will, for the present at least, be accepted.

The plants growing in the swamps naturally fell from time to time into the slightly acid water which surrounded them and because of this condition are partially preserved in the form of peat that today can be seen in almost every swamp in this country. Peat, as it lies in the swamp, is made up of about 10 per cent. of vegetal and mineral matter and 90 per cent. of water which is so intimately associated with the plant tissues that it can be separated from them with difficulty. As the vegetal material is different in different parts of the swamp, depending on the conditions and the

kind of plant material being deposited, the resulting peat will differ in appearance and in chemical composition. Thus the woody parts of the plants will make the ordinary coal and the seeds, spores and spore cases will, in due course of time, make cannel coal. These differences are, however, slight and for the present will be ignored.

In course of time the swamp with its layer of peat many feet in thickness may, under the influence of earth movements, subside below its former level, and the accumulated vegetal material may be submerged. In this condition the old swamp becomes a basin of deposition and the streams flowing into it will soon cover the peat with layers of sand or mud, and, in the course of time, the swamp may be completely obliterated.

In this condition the coal-making process goes on and is accelerated or retarded by the general geologic conditions that prevail. It seems to the writer quite evident that the vegetal material will undergo many changes and that these changes will have some sort of order or sequence. If that is true, they may be regarded as stages in the process of coal-making, and they also mark stages in the metamorphism of the material. The writer will now attempt to picture these stages, as he conceives them to have taken place.

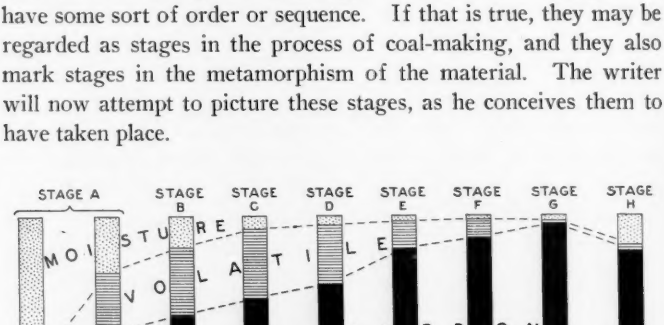


FIG. 4. Diagram showing the chemical composition of the coal in the various stages of metamorphism.

*Stage A.*—Stage A (Fig. 4) in the metamorphism of coal is necessarily the first stage that can be recognized and is charac-

terized by the transformation of peat into lignite, in some of its varied forms. The process by which this is accomplished is a simple one, consisting almost entirely of the compaction of the peat and the driving-off of its superfluous water by its own weight and the weight of sediment deposited on it. The reduction in the moisture content is from approximately 90 per cent. to about 37 per cent., as shown in Fig. 4. The resultant product is a more homogeneous mass of vegetal tissues than was found in the peat before the transformation occurred, and in this condition it is known as lignite. Lignite is generally brown in color and will crumble or slack on exposure to the weather. Because of this condition it can not safely be shipped in open cars and is liable to spontaneous combustion if pulverized or exposed in open stock piles.

So far as known this change is not produced by stresses other than those due to gravity, and as a rule the deposits lie far removed from mountain uplifts and from belts of weakness that are characterized by numerous earthquakes. It is evident that metamorphism has taken place in a relatively short time as most of the lignite beds in this country are of Eocene or Miocene age.

*Stage B.*—This stage is characterized by the transformation of the brown lignites described under Stage A to a glossy black coal with many of the characteristics generally regarded as marking bituminous coal. The change is principally due to continued compaction, but with no addition to the load by which it is produced, and by a slight element of lateral compression due to proximity of the areas of this kind of coal to mountain uplifts, that have been active in late Tertiary time. Presumably the effect of lateral compression is very slight indeed, but coupled with compaction, it is just sufficient to product a very decided change in the coal.

The principal change in the chemical composition is the reduction of the amount of moisture from about 37 per cent. in the lignites to 14.5 per cent. in the highest rank coals of Stage B. Although the moisture content is reduced, there is still a strong tendency to "slack" in most of these coals, a tendency even as

strong as that which characterizes the lignites of Stage A. Because of this condition, the coal can not be shipped in open cars without much "degradation" and danger of spontaneous combustion and it is equally liable to these troubles when stocked in open piles. There is very little change in the volatile matter of the coal, but a decided increase in the fixed carbon, which shows that the principal change has been one of condensation.

The coals of this stage are not mined in abundance, but are used to a considerable extent in the West for domestic heating and development of power. The most recent development is the demonstration by the Northern Pacific Railroad Company that coal of this type having a moisture content of about 24 per cent. can be used successfully for firing locomotives when the grates are adapted to it. It is used today for heavy traffic on the Mountain Division of this road with the greatest success.

In this stage should probably be included some of the high moisture coals of Iowa, northern Missouri, and northern Illinois which have had a somewhat different history from coals of a similar composition in the Rocky Mountain region. The coals of this type in the Mississippi Valley owe their present condition primarily to compaction but since the coals are of Carboniferous age the process has been in operation for many, many millions of years. It is possible, of course, that in addition slight stresses have developed from crustal disturbances in the regions surrounding the area in question but there is no indication that these stresses have been very active or that they have played an important part in the present condition of the coal. Until this can be shown to be a fact, the writer will regard the condition of these coals as due to compaction induced by the long continued pressure of overlying sedimentary beds. The moisture content of these coals ranges from 14.5 to 37 per cent.

*Stage C.*—This is the last stage in which the change in moisture is the most important factor. During this stage the moisture decreases from 14.5 per cent. to about 5 per cent. and beyond this stage it is fairly constant, at amounts ranging from 2 to 5 per cent. The coal changes little in appearance during Stage C, ex-

cept that in general it becomes harder as the moisture decreases and has a more blocky appearance as it comes from the mine. At some point in this stage not yet accurately determined the "slacking" property disappears and the coals near the upper limit will stand exposure in almost any kind of weather without appreciable deterioration. Near the bottom limit they "slack" considerably, but the "slacking" does not seriously interfere with their commercial value.

Judging from the location of coals of this stage, their peculiar properties are to be attributed first to continued compaction from Stage B, and secondly to slight crustal movements by which the rocks in adjacent fields have been deformed and the lateral stresses have been felt to a limited extent by the coals during Stage C. Such undoubtedly has been the case with the highest rank coals of western Kentucky, and of the southernmost fields in Indiana, Illinois, and Missouri which were mildly affected by the upraising of the Ozark Dome and the formation of minor rock folds. In the Rocky Mountains and the Great Plains the coals of this stage show evidence of having been affected by slight stresses which were produced by disturbances in the mountains proper but with diminishing intensity in the adjacent coal fields Coals belonging to this stage also occur along the western border of the Appalachian basin in Ohio where they contain from 5 to 10 per cent. of moisture and have felt to only a slight extent the stresses which produced the folds in the rocks further to the southeast.

In this stage the volatile matter of the coal has not been appreciably changed but the fixed carbon has been increased about 10 per cent. In the Mississippi Valley the coals of Stage C are regarded as the standard of excellence for domestic use, power production, and general heating purposes.

*Stage D.*—In the stages so far described the principal index of change is the decrease in the moisture content due to compaction, and the pressure that caused this change has been so slight that it produced no appreciable effect upon the containing rocks. From the beginning of Stage D compaction is slight compared with the compressive stresses set up by forces that caused the

deformation of the rocks, and its results are lost sight of in the great changes that have been produced by the more powerful agent.

In every coal field with which we are acquainted the coals of Stage D are associated with deformed rocks, gently folded at the lower limit but increasing in degree of deformation as time goes on until at the end of the stage deformation is considerable and the coal has been materially altered. On the diagram, Fig. 1, showing the change in composition of the Pittsburgh bed, the coal lying west of Chestnut Ridge or west of and including that of the Connellsville coking basin, belongs to Stage D and the structure line shows that the rock folds in this part of the section are slight, —at least as compared with those lying farther to the east.

Stage D is a very important stage in coal transformation, as it includes most of the high volatile or gas-making coals as well as much of the best coking coal of the Appalachian and Mississippi Valley regions. It includes also the coking coal of the Trinidad-Raton field of Colorado and New Mexico and also small areas of coking coal in western Colorado, Utah, and Washington. In general the volatile matter is greatest in coals belonging to the early part of this stage and gradually diminishes in amount toward the close; on the other hand the fixed carbon increases steadily upward throughout this stage and continues far beyond its uppermost limit. The most significant feature is the change in the physical aspect of the coal. At the beginning of the stage the coal is generally hard and blocky, the size of the blocks obtained in mining being governed by the closeness of the joint planes. At the beginning these planes are many inches apart but in an ascending direction they become gradually closer and closer until, near the close of the stage, they are so close that the coal tends to break along the cleavage planes rather than along the bedding planes, as is the case of the coals in the early part of the stage.

Although the coal in this stage is manifestly altered by metamorphism, the rocks associated with the coal show very little effect of pressure and that which does appear is mainly in the form of a slightly greater induration of the sandstones of this stage than of

those in association with the coals of any earlier stage. So far as the writer is aware no geologist has reported any development of slaty cleavage in the rocks associated with these coals and it seems reasonably certain that none occurs.

*Stage E.*—The coals of Stage E are probably as markedly differentiated from the coals of adjacent stages in both their physical and chemical characteristics as any in the entire range of coals. They are known in the trade as "low volatile," "smokeless," or "semibituminous" coals because their volatile content is much lower than any of the coals that hitherto have been considered. They are regarded as some of the best steaming coals of the world, whose heating value runs as high as 14,380 B.t.u's. Their content of volatile matter ranges from 15 to 26 per cent. and the fixed carbon from 65 to 77 per cent. in a normal coal with 6 per cent. of ash.

Although the chemical composition of these coals is quite distinct, their physical properties also serve to differentiate them from the coals of a higher stage and to a certain extent from those in a lower stage of development. Cleavage is developed in them to a great extent, in fact the coal is so friable that a lump may be crushed in the hand and, in mining, much of the coal comes to the surface in small lumps or is crushed to small fragments; but no matter how small the fragments may be, each is a perfect prism and generally as pure as the best lump coal.

This coal occurs in limited areas; such as the Pocahontas and New River fields of West Virginia and Virginia, the Georges Creek field of Maryland, and the Cambria, Clearfield, Somerset and Broadtop fields of Pennsylvania; a small field on Lookout Mountain in Georgia just south of Chattanooga; and a field of the same kind of coal in Arkansas and Oklahoma. There is a small amount in the Western States but it is scarcely worth mentioning here.

The rocks enclosing the coals of this stage are not very much contorted or folded. They generally lie in open synclines which are only slightly upturned on the rims, but in all cases they closely adjoin much more disturbed areas. They may be cut by more

joint planes than those of an earlier stage, but there are no reported cases of the development of slaty cleavage in them. In fact, the only observable difference in the associated rocks is that in passing eastward in the Appalachian region the sandstone becomes more and more indurated, but the change is so gradual that probably it can not be measured and therefore can not be used in the establishment of stages of metamorphism.

*Stage F.*—When the highly cleaved, low volatile coal of Stage E is subjected to much more severe pressure which usually results in pronounced rock folds, there is produced in the coal a very decided physical change by the recementation of the small prisms into a fairly homogeneous and resistant mass that is strikingly different from the coal of the lower stage. Curiously enough this great physical change is not accompanied by any marked chemical difference and consequently the two coals can not be separated on the basis of their chemical composition. Fortunately the physical difference is so great that it can be depended on to distinguish one coal from the other. This process of recementation marks the first stage in the transformation of bituminous coal into anthracite. There is no generally accepted name for the coal of this stage. Rogers, in the early days, called the coals of Stage F, "semi-anthracite," but this term is objectionable as it implies that the coal is only half as good as anthracite. It may be only half as hard, but its heating value,—all other things being equal—is greater than the standard anthracite. Because of this objection the word is inappropriate but no other name has been suggested that is generally acceptable.

This stage of coal occurs in small basins generally at some distance from the coals of bituminous rank, but nearer and sometimes in close association with the coal of anthracite rank. The distribution of this kind of coal indicates clearly that, while it has suffered greater deformation than the coals of the bituminous rank, it has not been so severely folded nor suffered such great compressive stresses as has the anthracite coal in the main fields of northeastern Pennsylvania. In a general way it is distinctly different from standard anthracite, but lack of reliable chemical

analyses makes it impossible at the present time to say with any degree of certainty just where the line separating them should be drawn.

*Stage G.*—The coal of this stage is so well known that it needs little or no description. It is the standard Pennsylvania anthracite which is characterized by its great hardness, metallic luster, and generally conchoidal fracture. Chemically it is noted for the small quantity of volatile matter it contains and for the great amount of fixed carbon, which runs as high as 95 per cent. in some cases in the ash-free form of analysis. This coal has been so severely compressed that it has lost almost all trace of its original bedding and the joint planes are much more pronounced than the bedding planes. The associated rocks also show signs of having been subjected to very severe stresses. The sandstones are greatly indurated, the shales are hardened and in some places show signs of the development of slaty cleavage. It is only a short distance from the Southern Anthracite Basin to the well-known Slate Belt where slate has been quarried since the early development of this region. Altogether, the evidence is fairly conclusive that the anthracitic stage of development of the coals can be definitely correlated with decided change in the enclosing rocks and thus the evidence afforded by the coal can be definitely tied to the degree of rock metamorphism which results in the development of slaty cleavage.

*Stage H.*—There is undoubtedly a stage beyond that which is designated as Stage G, but it is little understood and has only slight bearing upon the subject here being considered. The only known representative of this stage is the coal found in Rhode Island and in adjacent localities in Massachusetts. The material is generally graphitic in character and has evidently been subjected to very intense stresses and probably for a very long period of time. It is interesting as being the final or uppermost member of the series of coals that has yet been identified as such, but its bearing on the subject in hand is so remote that it will not be considered further.

RESUMÉ

If the evidence presented in the body of this paper is accepted, there seems to be no question that eight stages in the metamorphism of coal can be recognized and explained by the processes that have been active in the earth coincident with the development of plant life on the land; and that at least six of these stages have left few if any marks on the composition or physical appearance of the sediments associated with the coal, therefore, they may be classed as incipient stages of rock metamorphism.

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# HYDROTHERMAL OXIDATION AND LEACHING EXPERIMENTS; THEIR BEARING ON THE ORIGIN OF LAKE SUPERIOR HEMATITE–LIMONITE ORES.

JOHN W. GRUNER.

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## INTRODUCTION.

IT has previously been suggested by the writer [1] that the hematite ores of the Soudan formation of the Vermilion range had been leached of silica and oxidized by hot ascending waters from a large basic magma. Since then a large number of experiments

[1] Gruner, John W., "The Soudan Formation and a New Suggestion as to the Origin of the Vermilion Iron Ores," ECON. GEOL., vol. 21, pp. 629–644, 1926.

have been performed which show that minerals containing ferrous iron can be oxidized by water or steam in the absence of air at temperatures as low as 150° C. Even magnetite is oxidized at temperatures below 250° C. Other experiments which were made show that the solubility of silica in hot water is very great between 200° C. and 300° C. These results lend strong support to the hydrothermal hypothesis for the origin of the Vermilion ores and dispose the writer to extend his hypothesis to the other districts of the Lake Superior region. He realizes, however, that some bodies may have originated according to the hypothesis at present generally accepted, namely, that cold descending ground waters oxidized and leached the iron protores. This hypothesis will be referred to as the "weathering hypothesis" in the following pages.

The writer is indebted to Dr. W. H. Emmons, Dr. F. F. Grout, Dr. G. A. Thiel and Dr. G. M. Schwartz for the great interest they took in the progress of this work and for their criticisms. He also received valuable information from a number of geologists and mining engineers of the Lake Superior Region, especially from Dr. C. J. Muller of the Oliver Iron Mining Company and Mr. E. L. Derby, Jr., chief geologist of the Cleveland Cliffs Iron Co. Dr. R. B. Ellestad, chemist of the Rockefeller Foundation National Laboratory for Rock Analysis University of Minnesota, made valuable suggestions in connection with the experimental work and also carried out some of the determinations of ferrous iron in Table III. The experimental work was largely financed by the Graduate School of the University of Minnesota.

## THE LEACHING OF SILICA FROM THE IRON FORMATIONS.

The silica in the iron formations at the time of leaching was in the form of chert, quartz, jasper, and ferrous silicates of somewhat uncertain composition. The proponents of the weathering hypothesis have assumed that descending cold waters were high in alkalies, and alkali and alkaline earth carbonates. In this way they sought to overcome the difficulties attendant upon the solu-

tion of large quantities of chert, quartz, and silicates. These waters supposedly had drained from large areas covered with acid or basic igneous rocks from which alkalies or alkaline earths could easily be extracted.

It has been demonstrated many times[2] that carbonate and similar solutions at room temperature will dissolve $SiO_2$ to the extent of possibly 40 parts per million under the most favorable conditions but it has not been shown that ground water coming from areas of alkaline rocks is not already saturated with $SiO_2$. In other words the writer is of the opinion that ground water will usually become saturated with $SiO_2$ at the same source where it obtained its alkalies and alkaline earths in the decomposition of silicates.

Another postulate is met in the literature to explain the leaching by the weathering hypothesis. The silica which now is largely in the form of finely crystalline quartz is supposed to have been chert at the time of ore concentration. In this way the improbability of the removal of enormous masses of quartz and jasper is avoided. The field evidence, however, on the Vermilion and Marquette ranges at least, indicates that most of the silica was already in the form of quartz and jasper when it was attacked.

One also find the statement that the solvent power of ground water increased on its descent. This is said to have been due to an increase in $CO_2$ content in the water with increasing hydrostatic pressure. The writer cannot find any experimental evidence to the effect that either pressure or increase of $CO_2$ increases the solubility of $SiO_2$ in water markedly unless it be in the case of silicates, especially olivine or serpentine. But postulating even such an increase it is obvious that in the iron formation most silica would be dissolved high up near the surface with gradual decrease of solution dissolving below. Much silica, however, should be precipitated on the ascent, assuming artesian conditions,

[2] For references see: Lovering, T. S., "The Leaching of the Iron Protores: Solution and Precipitation of Silica in Cold Water," Econ. Geol., vol. 18, p. 523, 1923. Gruner, J. W., "The Origin of Sedimentary Iron Formations," Econ. Geol., vol. 17, pp. 421–436, 1922.

for gases could easily escape in the highly fractured iron formations. That there was such precipitation is unsupported by field evidence on the Mesabi, Gogebic, and Cuyuna ranges. The coarse vein quartz which is found cementing the relatively small quantities of hard ores of the Vermilion and Marquette ranges may, however, represent silica precipitated by ascending waters.

### EXPERIMENTS ON THE SOLUBILITY OF SILICA IN HOT WATER.

As it is generally known that water at temperatures up to 90° C. is relatively inefficient as a solvent of silica, experiments at 200° C., 250° C. and 300° C. were made. The writer could find no published data on experiments made at these temperatures.

#### *Materials and methods used.*

The minerals and rocks used are described below:

*Quartz,* colorless, transparent rock crystals from the Soudan mine of the Vermilion range. Crushed only in a steel mortar to pass through 100 mesh and held on 200 mesh. If quartz is ground to pass through 200 mesh some of it will pass through filter paper.

*Chalcedony.*—Loss on ignition 0.65 per cent. Crushed like quartz.

*Silica Gel.*—Hardened, glassy looking. Loss on ignition 9.9 per cent. Used in pieces of about 100 to the gram.[3]

*Greenalite rock* containing a little carbonate. Biwabik iron formation of the Mesabi range. From a drill hole in section 9, T. 58N., R. 17 W., Depth 170–175 feet.

*Greenalite Taconite* (with a trace of siderite).—Biwabik iron formation of the Mesabi range. From drill hole in section 9, T. 58 N., R. 18 W., Depth 381–386 feet. The greenalite rock and taconite were ground in agate mortars. Steel mortars were avoided because the material was also used in the experiments on the oxidation of ferrous iron.

*Duluth gabbro* from Duluth. Average composition. Ground in

[3] This material was kindly furnished by Professor L. H. Reyerson of the School of Chemistry, University of Minnesota.

steel mortar to pass through 100 mesh and held on 200 mesh.

The experiments were made in gold bombs enclosed in steel. The gold bombs were closed with discs of platinum. Gold discs would have been welded to the bombs at temperatures above 250° C. Even platinum had a tendency to alloy with gold when left longer than 24 hours. Except for slight modifications these bombs are like the one described by Foreman.[4] In a few experiments a gold bomb was used which permitted the very slow escape of gases through a valve. This bomb is described on a following page.

Distilled water was used. The water was boiled at least ten minutes until a few seconds before use to expel any air in it. The amount of water varied between 15 and 20 cc. The space above the water was carefully filled with $CO_2$, by bubbling $CO_2$ through the water before closing the bomb. Since the water was always hot no appreciable amounts of $CO_2$ could have been dissolved in it. The duration of each experiment with a few exceptions was close to 24 hours. The exact time is given in Table I. by the figure below and to the right of the one which gives the solubility in parts per million of water. Usually one gram of mineral was used. In those cases where only 0.1 gram was used in order to observe oxidation of the ferrous iron (as explained later) it is especially indicated in Table I. For analysis, the solutions were filtered and evaporated in platinum dishes. The residue was digested 15 minutes with dilute HCl (5 per cent.) and filtered. The $SiO_2$ was hydrofluorized. Where the amounts of $SiO_2$ seemed to be too high or too low, duplicate bomb experiments were made.

The left side of Table I. shows the experiments in the closed bomb. The right side gives the experiments in the bomb with the valve. The latter experiments lasted only a few hours because, due to the slow escape of the steam, the 25 cc. of water used in each experiment would be reduced to about 10 or 15 cc.

[4] Foreman, F., "Hydrothermal Experiments on Solubility, Hydrolysis and Oxidation of Iron and Copper Sulphide," ECON. GEOL., vol. 24, p. 820, 1929.

in 7 to 24 hours, depending upon the temperature of the experiment. It is, of course, unknown how much $SiO_2$ was precipitated during the cooling of the bombs to room temperature (15 to 25 minutes). Rapid chilling of the bombs will result in damage to them due to the unequal contraction of the metals.

TABLE I.

SOLUBILITY OF $SiO_2$ IN WATER AT ELEVATED TEMPERATURES AND PRESSURES. PARTS PER MILLION. TIME IN HOURS.

| Mineral or Rock. | In Sealed Gold Bomb. | | | | In Gold Bomb with Valve. | |
|---|---|---|---|---|---|---|
| | 200° | 250° | 275° | 300° | 200° | 300° |
| Quartz (rock crystal). | 37<br>28 | 140<br>23 | | 958<br>24 | | 493<br>6 |
| $SiO_2$ Gel (artificial opal). | 800<br>20 | | | 1410<br>24 | 789<br>22 | |
| Chalcedony. | 151<br>21 | | | 899<br>21 | 295<br>21 | |
| Greenalite 1.0 g. | 86<br>23 | 625<br>23 | | 400<br>21 | | |
| 0.1 g. | 22<br>20 | 266<br>22 | 428<br>24 | 365<br>23 | 104<br>20 | 395<br>7 |
| Greenalite-taconite. | 115<br>23 | 323<br>18 | | 380<br>15 | | |
| | | 388<br>45 | | | | |
| Gabbro | | | | 114<br>24 | | |

*Results of experiments.*

Notwithstanding the short time of the experiments large amounts of $SiO_2$ went into solution. The silica gel dissolves rapidly even at 200° C., but quartz is little attacked at that temperature. At 300° C. it is about equal to that of chalcedony and approaches that of silica gel. It is probable that at somewhat higher temperatures and longer time all forms of relatively pure $SiO_2$ become equally soluble.

The relatively low solubilities of greenalite and greenalite-taconite at 300° C. are somewhat surprising. There may have been more silica in solution, since on close inspection much opal-like, colorless $SiO_2$, in the form of scales, could be seen on the filter paper in some experiments. It is possible that these flakes were precipitated during the cooling of the bombs.

Some experiments were made on the solubility of $SiO_2$ from Duluth gabbro as compared with quartz. Three different carbonate solutions were tried on this rock and on quartz and the results are recorded in Table II.[5] The quartz, as will be seen, is

TABLE II.

SOLUBILITY OF $SiO_2$ IN CARBONATE SOLUTIONS AT 300° C. AND CORRESPONDING PRESSURES. PARTS PER MILLION.

| Time. | 24 Hours. | 25 Hours. | 23 Hours. | 24 Hours. |
|---|---|---|---|---|
| Mineral | $NaHCO_3$ 2.0 g. in 15 cc. $H_2O$ * | $NaHCO_3$ 1.0 g. + $CaCO_3$ 0.2 g. in 15 cc. $H_2O$ * | $NaHCO_3$ 1.0 g. + $CaCO_3$ 0.2 g. + $MgCO_3$ 0.2 g. in 15 cc. $H_2O$ * | Distilled water. |
| Quartz (rock crystal). | 742 | 621 | 777 | 958 |
| Duluth gabbro. | 64 | 50 | 20 | 114 |

* Solutions saturated with $CO_2$ at room temperature.

much more soluble than the $SiO_2$ from the gabbro. This was to be expected in the carbonate solutions if the relation of the common ion effect utilized in analytical chemistry for the suppression of the solubility of compounds is valid at elevated temperatures. In other words, in solutions containing ions of the same metals as those in the silicates to be dissolved, $SiO_2$ from these silicates should be less soluble than in other solutions.

[5] The carbonate solutions were saturated with $CO_2$ before use. They were under $CO_2$ pressure when the bombs were opened even after cooling to nearly freezing temperature. This probably was due to the partial decomposition of $NaHCO_3$.

The low solubility of the $SiO_2$ from the basic gabbro has a direct bearing on the author's hypothesis in which he assumes that aqueous solutions came from basic magmas and attacked the chert and quartz of the iron formations without, however, dissolving much $SiO_2$ from the numerous associated basic dikes which were only partly hydrothermally altered. In general such carbonate solutions, charged with $SiO_2$ after penetrating the iron formations, probably would not precipitate any minerals other than quartz and carbonates when approaching the surface. Their temperatures and compositions (especially their lack of Al and K) would not permit the deposition of silicates, not even of zeolites, on a large scale, though small amounts of adularia, mica, stilpnomelane, and chlorite have been reported in veins in the ores.

### OXIDATION OF MINERALS CONTAINING FERROUS IRON.

The oxidation of ferrous minerals may be observed in many regions to the depth of 10 to 20 feet. Complete oxidation except in some laterites and gossans is rare even to that depth. A mineral such as magnetite is not easily oxidized under any conditions, as evidenced by the great abundance of this mineral in outcrops of iron formations the world over. It is also a conspicuous constituent in stream and desert sands. In laterites, magnetite is often the only mineral that is not oxidized, as has been shown by Harrassowitz [6] in his extensive researches.

Leith and Mead [7] also mention magnetite as still present in the Cuban iron ores which have weathered from serpentine. Where we see magnetite attacked by weathering it is converted to limonite. It is probably first taken into solution by acid waters and the iron then precipitated by hydrolysis.

When the writer described the martite ore bodies of the Mesabi range,[8] Newland [9] was the first one to express doubt as to the

[6] Harrassowitz, H., "Laterit," Berlin, 1926, p. 346.

[7] "Origin of the Iron-ores of Central and Northeastern Cuba," *Trans. Am. Inst. Min. Eng.*, vol. 42, pp. 91, 93 and 99, 1912.

[8] Gruner, J. W., "Paragenesis of the Martite Ore Bodies and Magnetites of the Mesabi Range, Minnesota," ECON. GEOL., vol. 17, pp. 1–14, 1922.

[9] Newland, D. H., ECON. GEOL., vol. 17, p. 299, 1922. (Discussion.)

possibility of martitization of magnetite by cold ground water. The writer has shown in a number of papers[10] that magnetite is one of the most resistant minerals under oxidizing conditions. He knows of no occurrence of martite (excepting the Lake Superior iron ores as explained by the weathering hypothesis) where the presence of martite could not be more readily explained by thermal or hydrothermal activity than by the action of cold water.

Ferrous silicates oxidize more readily. But even in such favorable rocks as serpentine, which dissolves easily, long periods are required to produce oxidation to a depth of 30 to 40 feet. Iron carbonate oxidizes fairly readily near the surface, as is usually shown by its chocolate brown surface layer. Even in this mineral, oxidation usually will not reach very deep unless assisted by acid waters. This may be observed in a number of places on the Canadian shield where iron carbonate on glaciated surfaces is partially altered to a depth of possibly one inch.

It will be noticed that no mention has been made of the oxidation of iron sulphides. These minerals occur in the iron formations in negligible amounts except in a few places. The ores are very low in sulphur, a fact which precludes the assigning of any important rôle to the oxidation of sulphides with the attendant oxidizing action of iron sulphates and sulphuric acid.

When geologists proposed the weathering hypothesis in 1892,[11] the iron ores of the Lake Superior region had not been explored beyond a depth of a few hundred feet. Besides, it was thought that ores found at greater depth had been carried downward by orogenic movement after oxidation and leaching. This may be the case with a few ore bodies on the Marquette range but the great bulk of the deposits did not undergo such metamorphism as will be shown under a discussion of the individual districts. We know now that ore bodies exist at depths of 4000 feet on the Gogebic, 3000 feet on the Marquette and 900 feet on the Mesabi

[10] Gruner, J. W., "Magnetite-Martite-Hematite," ECON. GEOL., vol. 21, pp. 375–393, 1926. Also ECON. GEOL., vol. 21, pp. 629–644, 1926.

[11] Irving, R. D., and Van Hise, C. R., "The Penokee Iron-bearing Series of Michigan and Wisconsin," U. S. Geol. Surv. Mon. 19, 1892.

range. On the other ranges the ores developed extend to depths of 900 to 2000 feet. The deep ore bodies are in every respect similar to those that outcrop at the surface.

## EXPERIMENTS ON THE OXIDATION OF FERROUS MINERALS BY $H_2O$ AT ELEVATED TEMPERATURES.

In practically every textbook of chemistry one finds the following reaction:

$$3Fe + 4H_2O(steam) \leftrightarrows Fe_3O_4 + 4H_2.$$

This reaction is rapid at red heat. The reaction

$$3FeO + H_2O \leftrightarrows Fe_3O_4 + H_2$$

has also been studied above 600° C. in recent years.[12] It has been stated in geological literature[13] in connection with the oxidation of basalt flows that at high temperatures ferrous minerals oxidize to ferric minerals by the decomposition of $H_2O$. It occurred to the author that such reactions might start at temperatures near 200° C. or 300° C. Possibly catalytic agents could be found that promote the reactions at these relatively low temperatures. With this end in view about 100 experiments were made which prove that this reaction actually starts below 200° C. Some experiments will be described in detail.

### *Minerals and rocks used.*

Except in breaking large pieces into small pieces for subsequent grinding no iron tools were used in grinding to 200 mesh any of the minerals used in the oxidation experiments.

*Magnetite* from the lower cherty horizon of the Biwabik formation of the Mesabi range. Section 9, T. 58 N., R. 17 W. Depth 170′–175′. FeO = 30.84. Total Fe 68.07. This sample contains some siderite as impurity which by repeated boiling with

[12] Eastman, E. D., and Evans, R. M., "Equilibria Involving the Oxides of Iron," *Am. Chem. Soc. Jour.*, vol. 46, p. 888, 1924.

[13] Butler, B. S., and Burbank, W. S., "The Copper Deposits of Michigan," U. S. Geol. Surv. Prof. Paper, 144, p. 44, 1929. See also: Ferguson, J. B., "The Oxidation of Lava by Steam," *Jour Wash. Acad. Sci.*, vol. 9, p. 539, 1919.

very dilute HCl could not be removed. About 28.72 per cent. of FeO is in the magnetite and 2.12 in the siderite.

*Siderite,* cream colored, fine grained, from the Intermediate slate in the Adams pit, Mesabi range. FeO = 39.84. Total Fe = 31.60. The rest of the mineral is chiefly $CO_2$, $SiO_2$ and MgO.

*Siderite,* light brown, from Roxbury, Conn.

*Artificial magnetic oxide* manufactured by Binney and Smith, New York. This is extremely finely divided black magnetic oxide powder used for polishing purposes. FeO = 17.62. Total Fe = 67.05. It was used because it reacts much more rapidly than natural magnetite on account of its fine grain.

*Greenalite rock* described in the previous chapter. FeO = 26.57.

*Greenalite taconite* described in the preceding chapter. FeO = 26.59.

*Six polished pieces of drill core* containing abundant magnetite, from various localities of the Mesabi range.

*Experiments with superheated steam at atmospheric pressure.*

*Methods Used.*—A wide pyrex tube was passed through an electric tube furnace. One end of the tube was connected to a three liter flask (pyrex) in which steam was generated on an electric hot plate. The mineral was placed in the tube (in a porcelain boat if powdered) and steam passed over it. The temperature was measured with a mercury thermometer whose bulb was close to the mineral. In order to avoid the introduction of traces of air another three liter flask was connected to the steam generator by a syphon arrangement. When the steam generator had to be refilled (once a day), water was boiled in the second flask for ten minutes until all the air had escaped. Then the valve to the steam generator was opened and the boiling water was syphoned over under its own pressure. In this manner boiling in the generator did not stop for a fraction of a minute during the duration of the experiment. At the end of the experiments the specimens were cooled in an atmosphere of nitrogen. The results follow:

*Magnetite* begins to show oxidation to hematite after 5 days heating at 258° ± 3° C. Three drill cores were tried, all with the same result. A repetition of these experiments gave the same oxidation. Fig. 1, shows this oxidation after 7 days. Hematite always forms along the octahedral planes of magnetite and has no relation to any irregular areas of hematite that were in the sections before heating. In many cases the oxidation proceeds along outlines of former crystals of the rhombohedral system which were replaced later by magnetite. This oxidation is very similar to that produced artificially by heating polished specimens in the air and pictured by the writer in this journal.[14]

Powders of the Mesabi magnetite and artificial magnetic oxide begin to show slight color changes at 260° to 275° C. At 290° C. the black artificial oxide becomes mahogany brown within three days though retaining a considerable percentage of its FeO and its magnetism. The lowest temperature at which steam begins to oxidize magnetite is, of course, unknown, though it may be as low as 200° C.

*Greenalite and greenalite taconite* powders change from gray or greenish gray to brown at temperatures close to 250° C. and above. This change is very slow and not enough material was tried to make quantitative determinations of the changes. It is thought that limonite results near 250° C. and hematite near 300° C.

*Blue asbestos crocidolite* from South Africa begins to show very slight oxidation to red after ten days in steam at 258° C.

*Mesabi and Roxbury siderite* begin to oxidize to magnetite in steam at 180° C. At lower temperatures the results are not conclusive, for sometimes the siderite changes to brown without becoming magnetite. Above 200° C. the change to magnetite is relatively rapid. Many tests were made up to 300° C., always with the same result. Near 300° C. it was noticed that the magnetite formed began to turn from black to brownish red. Evidently after a grain had been changed completely to magnetite

[14] ECON. GEOL., vol. 21, p. 390, 1926.

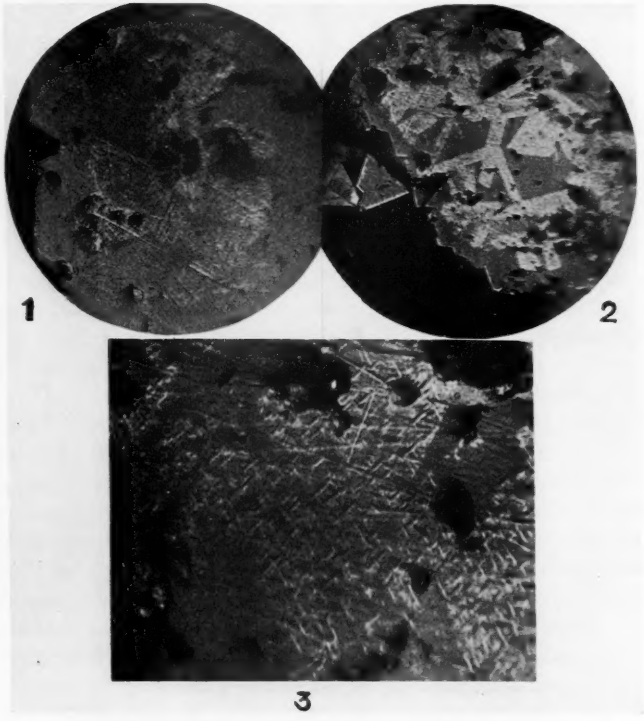


FIG. 1. Magnetite (gray) showing areas of incipient oxidation to hematite (light gray) produced by steam in the absence of air at 258° C. in seven days. The outlines of oxidation follow in part those crystals which were replaced by magnetite. × 400.

FIG. 2. Magnetite (gray) oxidized to hematite (white) by steam containing very minute amounts of HCl at 245° ± 5° C. in five days. × 400. Oxidation follows original crystals replaced by magnetite.

FIG. 3. The same polished section as in Fig. 2, showing the progress of oxidation along the octahedral planes of magnetite. × 800.

it began to oxidize to hematite only at a much slower rate than the siderite to magnetite. The two reactions are as follows:

$$3FeCO_3 + H_2O \longrightarrow Fe_3O_4 + H_2 + 3CO_2$$
(rapid)

$$2Fe_3O_4 + H_2O \longrightarrow 3Fe_2O_3 + H_2$$
(slow)

Influence of HCl on the rate and temperature of oxidation.

A series of experiments similar to those described were performed in which minute amounts of HCl were introduced with the steam. The HCl vapor was introduced into the steam by a small tube attached to a small flask containing a little concentrated HCl. A little nitrogen was passed through the small flask into the pyrex tube containing the mineral. The nitrogen gas carried small amounts of vapor of HCl with it. In order to free the medical nitrogen used from any traces of oxygen, it was bubbled through pyrogallic acid. The amount of HCl introduced depended entirely upon the flow of nitrogen. It probably did not exceed 1 cc. of concentrated HCl acid for 3 liters of steam. These minute amounts of HCl accelerated the oxidation noticeably and at the same time lowered the temperatures at which the reactions became perceptible. In the experiment with artificial magnetic oxide, for example, the oxidation became quite noticeable at 200° C. within 24 hours. Figs. 2 and 3 show polished sections which were subjected to this treatment 5 days at 245° $\pm$ 5° C. The HCl may have the following function:

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$
$$3FeCl_2 + H_2O \rightarrow 2FeCl_3 + FeO + H_2$$
$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6\ HCl.$$

It is possible, however, that the oxychloride of iron, FeOCl, appears in these reactions. Very little information is available on these reactions. Roscoe and Schorlemmer[15] state that $FeCl_2$ when heated in steam forms magnetic oxide. The temperature is not given. It will be noticed that the HCl is not used up in the reaction. Therefore in a geologic environment of quartz and

[15] Treatise of Chemistry, 1913, p. 1228.

iron minerals a very small amount could assist oxidation materially. This fact is also brought out in the bomb experiments below.

The behavior of siderite between 160° and 200° C. in steam in the presence of minute amounts of HCl is erratic. Sometimes

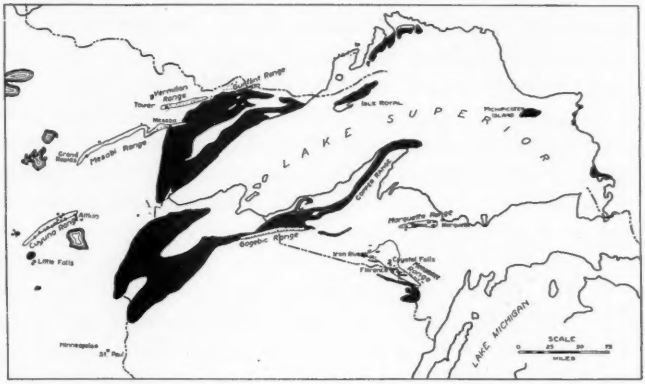


FIG. 4. Lake Superior region showing the distribution of upper Huronian and Keweenawan basic intrusives and extrusives (black). Due to the small scale, some had to be exaggerated. Where volcanic activity was intense only a few of the intrusives are shown.

magnetite will form between 180° and 200° C. At other times the siderite will turn to a limonitic substance. Below 180° C. but above 160° C., limonite seems to be the only product. Whether any changes take place below 160° C. is not known. A sample treated for three days at 150° C. did not show any alteration.

*Bomb experiments on the oxidation of ferrous minerals.*

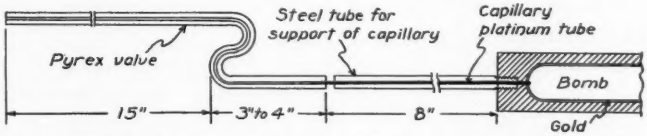


FIG. 5. Sketch of valve used with gold bomb in oxidation experiments.

*Methods Used.*—These oxidation experiments were made in a gold bomb provided with a valve, and with a capacity of 51 cc. Otherwise it is of the same construction as the one described under the silica experiments. The valve, which is sketched in Fig. 5, works on the same principle as one constructed by Dr. Fred Foreman and the writer, and described in this journal.[16] The capillary platinum tube has an inside diameter of 0.3 mm. and is soldered to the gold bomb with 22 karat gold. The pyrex tube is fused to the platinum capillary and filled with No. 600 alundum powder above the bend. The valve, including the upper three inches of the platinum tube, was outside the furnace during the experiments. At 300° C. about 25 cc. of $H_2O$ escaped through the valve in about 12 hours. At 200° C., 25 cc. needed about 36 to 48 hours. About 55 experiments were made in this bomb. In all experiments hot distilled water was employed which had been boiled 10 minutes just before use. $CO_2$ was bubbled through the water until the bomb was closed, great care being taken that no air was left in the bomb. For the quantitative determinations of FeO, standard titrating methods were used. Special care was taken that all analyses were made under exactly the same conditions. The original samples were run in duplicate or triplicate. Enough duplicates of the experiments were analysed to assure accuracy. 0.35 gram of the sample were analysed in each determination of the 0.5 gram used in each experiment.

Since some of the finest-ground material would often adhere to the inside of the bomb and could not be recovered with a rubber policeman, the percentage of oxidation found is probably slightly lower than the actual oxidation. The 2 mg. samples of artificial black magnetic oxide used gave no test for ferrous iron after the specified time. The magnetite obtained from siderite was so considerable in amount and easily tested qualitatively that no quantitative analyses were made.

In the experiments with HCl *one drop* of concentrated acid was used in each 25 cc. $H_2O$ put into the bomb. Due to the nature of the valve, the duration of the experiments varied much, but at

[16] ECON. GEOL., vol. 24, p. 835, 1929.

the end of each one given in the table, more than 1 cc. of water remained in the bomb.

*Experimental Results.*—In the experiments with siderite the change to magnetite is rapid above 200° C. These experiments were also repeated several times with Roxbury siderite. In sealed capillary pyrex tubes this reaction does not take place. Two experiments at 200° C. in which ferric hydroxide formed from siderite are recorded in Table III. In two more tests, however, under apparently the same conditions magnetite formed. The reason why ferric hydroxide forms in some experiments and magnetite in others, apparently under identical conditions, is not known. It is, however, almost certain that in nature conditions may be found for both of these reactions. At 175° C. with one drop HCl, magnetite was also obtained and at 150° C. with one drop HCl, a beautiful reddish brown scaly hydroxide formed in 74 hours. In this last test 100 milligrams of siderite were used. About 50 milligrams were oxidized to hydroxide, a surprisingly large amount for such a low temperature.

The oxidation of artificial magnetic oxide and natural magnetite in $H_2O$ between 250° C. and 300° C. is so slow that it cannot be determined quantitatively. Slight color changes indicate oxidation, however. If these experiments could be extended over many days instead of a few hours, oxidation would become accurately measurable. The addition of one drop of concentrated HCl to the $H_2O$ speeds up the reaction very much. Oxidation is obtained even at 200° C. with artificial magnetic oxide (Table III). On the Mesabi magnetite it is not noticeable, however, on account of the siderite contained in it which must be converted to magnetite first. Nevertheless, under the microscope one can observe a change to reddish brown in many grains of small samples treated at 300° C.

The silicates begin to oxidize in water at 200° C. The reaction becomes relatively rapid at 250° C., as shown in Table III. A drop of HCl speeds up these reactions. The color *always* changes to a limonite brown. No magnetism was developed in any of the greenalite taconite samples. It is thought, therefore,

TABLE III.

THE OXIDATION OF FERROUS IRON BY $H_2O$ IN A BOMB PROVIDED WITH A VALVE.
TIME IN HOURS. OXIDATION GIVEN IN PER CENT. OF TOTAL FeO PRESENT.

| Mineral Used. | 200° C. $p$ = 15.3 atm. | | 250° C. $p$ = 39.2 atm. | | 300° C. $p$ = 84.7 atm. | |
|---|---|---|---|---|---|---|
| | Dist. $H_2O$. | $H_2O$ + 1 Drop HCl. | Dist. $H_2O$. | $H_2O$ + 1 Drop HCl. | Dist. $H_2O$. | $H_2O$ + 1 Drop HCl. |
| Mesabi siderite FeO = 39.84. | Limonite color | Limonite color | Magnetite | Magnetite | Magnetite | Magnetite |
| Time. | 9 | 24 | 18 | 5 | 12 | 6 |
| Per cent. FeO oxidized. | 1.60 | 5.29 | | | | |
| Artificial magnetic oxide FeO = 17.62. | No change | 2 mg. used oxidation to hematite | 2 mg. used no visible change | 2 mg. used oxidation to hematite | | Hematite red |
| Time. | 24 | 24 | 24 | 24 | | 12 |
| Per cent. FeO oxidized. | | Complete | | Complete | | 10.38 |
| Magnetite FeO = 30.84. | No change | | No visible change | | No visible change | Dark brown spots |
| Time. | 48 | | 24 | | 12 | 12 |
| Per cent. FeO oxidized. | | | | | | 5.13 ** |
| Greenalite rock FeO = 26.57. | | | Light brown | | Light brown * | Light brown |
| Time. | | | 15 | | 9 | 12 |
| Per cent. FeO oxidized. | | | 0.94 | | 6.22 | 8.62 |
| Greenalite taconite FeO = 26.59. | Yellowish brown | Light brown | Light brown | Light brown | Light brown | Light brown |
| Time. | 18 | 48 | 15 | 23 | 10 | 6 12 |
| Per cent. FeO oxidized. | Trace | 4.81 | 1.65 | 3.38 | 1.39 | 4.17 5.60 |

* A trace of $MnO_2$ and a pinch of NaCl were added in this experiment.
** This oxidation must be ascribed to the siderite in the sample.

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stituted
experim
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that oxidation produces ferric hydroxide. Scales of opal-like silica are often found in the oxidized samples.

In all these experiments $FeCl_2$ or $FeCl_3$ could have been substituted for HCl without changing the end product. In the bomb experiments with water scarcely a trace of iron could be detected in the solutions with KCNS after addition of a few drops of $HNO_3$. The solutions of the experiments to which a drop of HCl had been added showed a few parts of Fe per million at the most.

The stability of limonite in the presence of water was tested at 250° C. and 300° C. in sealed thick-walled pyrex tubes. At 250° C. limonite showed no change. At 300° C. it was found that limonite in the tube above the water turned a brilliant red, whereas the limonite under water remained unchanged. The time of the experiment was 21 days. On analysis it was found that the whole sample in the tube contained 5.95 per cent. volatile matter after drying at 105° C., and the ignition loss of the original material after drying at 105° C. was 12.13 per cent. This very peculiar behavior of ferric hydroxide at these temperatures will be investigated further. It is probable, however, that as Van Bemmelen [17] pointed out long ago, limonite is stable in the presence of water and under corresponding pressures at temperatures which approach 300° C.

| Per cent. FeO oxidized. | Trace | 4.81 | 1.65 | 3.38 | 1.39 | 4.17 | 5.60 |
|---|---|---|---|---|---|---|---|

* A trace of $MnO_2$ and a pinch of NaCl were added in this experiment.
** This oxidation must be ascribed to the siderite in the sample.

### PERIOD OF MAXIMUM ORE CONCENTRATION.

In a discussion of the agencies that oxidized and leached the protores it becomes necessary to inquire into the rate and time of maximum concentration. Under the weathering hypothesis, this depends largely on the rate of erosion of the ore bodies. An arithmetical example shows how fast an ore body might have formed under very favorable conditions.

Assuming a solubility of $SiO_2$ of 10 parts per million (in addition to any $SiO_2$ brought from the surface) and an average porosity of 20 per cent. in the iron formations, this pore space would have had to be filled one million times before all the $SiO_2$

[17] Roscoe and Schorlemmer, "Treatise of Chemistry," 1913, p. 1222.

could have been removed. If we postulated a velocity of 500 feet a year [18] for water flowing through an ore body half a mile long, the leaching of the silica would have taken over five million years. This is not in itself an excessive span of time, but if this example is applied to ore bodies over one mile in length, one wonders why the rate of erosion during concentration was not greater than the rate of leaching, especially since the ores are softer than the associated rocks.

Van Hise and Leith [19] think that "the ore deposits formed would continue to pass downward *pari passu* with denudation." Such migration would necessitate the continuance of the same favorable conditions for the formation of the ore over geologically very long periods of time. This seems to be in conflict with the assumption of special conditions of aridity (or semi-aridity) and topography by Leith,[20] Hotchkiss,[21] and others.

As will be shown later, oxidation and leaching on a grand scale began some time toward the end of the upper Huronian period. That it was well advanced, if not almost completed at the end of Keweenawan time, is recognized by most investigators. Van Hise and Leith [22] write:

> In the pre-Cambrian period of mountain making and denudation the ore deposits probably reached their full development, and indeed they may during the latter part of this ancient time have been of greater magnitude than they are at present, although not so rich. In the Menominee district the upper Cambrian sandstone and the Ordovician limestone cap the Huronian formations and even some of the ore deposits. The upward extension of the iron-bearing formation was removed before upper Cambrian time. It is clear, therefore, that the main concentration of iron oxide for these deposits must have taken place in pre-Cambrian time. The basal conglomerates of the Cambrian carry ore fragments from previously altered formations. If, as is probable, Cambrian and Or-

[18] Slichter, C. S., "The Motions of Underground Waters," U. S. Geol. Survey Water Supply Paper 67, p. 27, 1902.

[19] Van Hise, C. R., and Leith, C. K., "The Geology of the Lake Superior Region," U. S. Geol. Survey Mon. 52, p. 558.

[20] Written communication.

[21] Hotchkiss, W. O., "The Geology of the Gogebic Range and its Relation to Recent Mining Developments," Eng. and Min. Jour., vol. 108, p. 578, 1919.

[22] Mon. 52, p. 558.

dovician or Silurian strata capped the beds in other iron-bearing districts of the Lake Superior region, it is all but certain that ore concentration was equally advanced in these other districts, although where erosion has extended farther below the Paleozoic than in the Menominee district later events have had a greater influence upon the present conditions of the ore deposits.

Since it is impossible to reconstruct all the post-Keweenawan history of the region, we may at least make an attempt to inquire into the leaching ability of the ground waters which are known to circulate through iron formations today. The analyses of iron mine waters of the region (two in Mon. 52, p. 543, with 22.35 and 8.35 parts of $SiO_2$ per million respectively, and one by the writer [23] with 31.5 parts) resemble those from glacial drift [24] and other ground water sources in general so closely that one is forced to the conclusion that any ground water entering the iron formation today takes hardly any additional silica into solution. These analyses, then, support to some extent the belief that the ore deposits reached their full development at the end of the Keweenawan period.

## GROUPING OF THE DEPOSITS ABOUT THE LAKE SUPERIOR GEOSYNCLINE.

Is it a coincidence that the oxidized and leached deposits occur grouped about the Lake Superior geosyncline (Fig. 4)? It can not be solely due to the iron formations having this distribution, for the formations occur in other parts of the pre-Cambrian

[23] There may be added an analysis of water from a mine working in taconite in the Fayal mine of the Mesabi range. The water was collected and filtered in the mine by the writer. Analyst I. W. Geiger, University of Minnesota.

Analysis in parts per million:

| | | | |
|---|---|---|---|
| Total solids (110° C.) | 232.6 | Ca | 26.7 |
| Organic matter | 29.2 | Na and K (as Na) | 17.6 |
| $SiO_2$ | 31.5 | $SO_4$ | 25.6 |
| Fe | 8.5 | Cl | 13.2 |
| Al | 1.3 | $CO_3$ | 67.0 |
| Mg | 17.1 | | |

The large amount of iron is evidently due to the action of organic matter.

[24] See for example, Allison, I. S., "The Subsurface Geology and Water Supply of Northwestern Minnesota," Minn. Geol. Survey Bulletin, in press.

shield and of North America. If weathering produced deposits in the Lake Superior region, why was such a universal geologic process not more active in the other iron formations? Is one not justified to look for a possible cause to the tremendous volcanic upheavals which were responsible for the geosyncline,[25] especially since the oxidation and leaching of the ores seems to fall principally into this epoch. If this postulate is correct it should be possible to find leached and oxidized ores in similar geologic settings elsewhere in the world. There is an analogous one in South Africa where vast areas were intruded by the Bushveld complex. Investigators have referred to the geological similarity of these two regions and some of them, especially P. A. Wagner,[26] have pointed out that the Lake Superior ores have their counterparts in those of South Africa. In his recent memoir he has listed many features which the South African ores have in common with the ores under discussion. Wagner accepts the weathering hypothesis.

The ores in general are more like those of the Marquette or Vermilion ranges than any others. They seem to be developed preferably at the contacts of ferruginous cherts and dolomites, in places replacing the latter. Much secondary hematite was brought in by solutions. The hematite is specular. Wagner[27] states: ". . . in rather rare instances where the layers of secondary hematite consist largely or entirely of comparatively coarsely crystallized specularite, there is always clear evidence of hydrothermal action in the form of patches and veins of quartz exhibiting a crustified structure." This rather common occurrence in Vermilion and Marquette ores has been thought by the proponents of the weathering hypothesis to be of either cold water or metamorphic origin.

The Blink Klip breccia ores of the Griqualand West are deposits in which the underlying dolomite was dissolved, causing slumping and brecciation of the overlying iron formation. The

[25] Hotchkiss, W. O., "The Lake Superior Geosyncline," Geol. Soc. Am. Bull., vol. 34, pp. 669–678, 1923.

[26] Wagner, P. A., "The Iron Deposits of the Union of South Africa," Union of So. Africa Geol. Surv. Mem. 26, pp. 144–188, 1928.

[27] *Op. cit.*, p. 152.

silica was leached and largely replaced by specular hematite. The ore as a whole, however, is porous and closely resembles the Vermilion ore, according to Wagner.[28] In describing the type locality he comes to the conclusion that hydrothermal action may have played a part at some stage of the concentration of the ore. Though the Blink Klip deposits are 300 to 400 miles distant from the others of the Bushveld proper, many diabase and dolerite intrusions are found in their vicinity.

The ores of the Krivoy Rog district of South Russia have certain features [29] which resemble the Lake Superior ores. Since the geology is highly complex and relatively few outcrops exist the geology is not known very well. The ores which the author had had an opportunity to see are fine-grained banded hematite and martite. They occur as lenses in the steeply dipping iron formation, which is a member of a series of schists, slates, and quartzites. "Greenstone" masses and diorite and diabase dikes cut the iron formation in numerous places.

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[28] *Op. cit.*, p. 182.

[29] Trasenter, Paul, "L'industrie charbonniere et siderurigique de la Russie meridionale," *Revue Univ. des Mines*, Liege, 1896.

Macco, A., "Ubersicht der geologischen Verhältnisse von Krivoi Rog in Südrussland, under besonderer Berücksichtigung der Eisenerzlager," *Zeit. f. prakt. Geol.*, 1898, pp. 139–149.

(*To be concluded in next number*).

# SOME PROPERTIES OF LIMESTONE AS A RESERVOIR ROCK.[1]

W. V. HOWARD AND W. W. LOVE.

## INTRODUCTION.

THE experiments described in this paper were carried on in an attempt to find out something of the behavior of oil in limestone reservoirs and to enable us to form some conclusions as to the recovery of oil from limestone.

In the first experiments performed, attempts were made to pass oil through blocks of limestone under low pressure differentials. Oil was sucked through a limestone block by means of an aspirator and it was found that the gravity of this oil was lowered by an amount greater than was expected and also greater than took place when oil was boiled under the same pressure in the absence of limestone. The rock was found to be stained by a light oil which had the odor of kerosene, indicating a strong possibility that some fractionation of the crude had taken place. Because of the vaporization of most of the oil which had passed through the block, this experiment had no quantitative value.

Attempts were then made to pass oil through limestone under small pressure differentials under conditions where the oil could be collected, but without satisfactory results. Either the oil did not pass through the limestone at all, or else it passed through so rapidly that it could not be controlled. Nor was it possible to observe any effect on such oil as did penetrate the rock.

[1] Presented before the Society of Economic Geologists, Charlottesville, Va., April 24, 1930. This paper contains preliminary results obtained in an investigation of limestones as reservoir rocks, listed as Project No. 23 of the American Petroleum Institute Research. Financial assistance in this work was received from a research fund donated by the Universal Oil Products Company to the American Petroleum Institute. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

Because of the unsatisfactory results obtained, and also because of the fact that had satisfactory results been obtained, it would be impossible to reproduce them with other blocks of limestone due to the great variation in size of openings in this rock, it was decided to use crushed limestone. The uniformity which is gained by this change in procedure may not be typical of natural conditions, but it is hoped that some application of the results obtained may be made.

### MIGRATION OF OIL THROUGH CRUSHED LIMESTONE.

In the first experiment with crushed limestone a glass tube one half inch in diameter and about four feet long was filled with crushed limestone sized between 9 and 16 mesh. The tube was placed upright and crude oil poured into the top. The crude oil used in this experiment was a heavy black oil from the Embar formation of Wyoming. It had a gravity of 24.8° A.P.I. Due to its high viscosity it passed through the limestone rather slowly.

The first oil to pass through the tube had a gravity of 26.6° A.P.I. but as more oil was passed through, the gravity of the oil steadily decreased to 24.3° A.P.I. At this point the tube was flushed out with water and the oil which had adhered to the limestone was collected and tested and found to have a gravity of 22.5° A.P.I.

This experiment was repeated a second time but in this case a lighter crude from the Trenton limestone of Ohio was used instead of the heavy Embar crude. The Ohio crude had a gravity of 39.6° A.P.I. The first oil to pass through the tube had a gravity of 40.2° A.P.I. and the oil which passed through later steadily decreased in gravity until that which passed through was nearly similar in character to the original crude.

As the limestone becomes thoroughly coated with oil, the oil passing through does not come in contact with the rock, but slips along over a film of oil. No further change in the oil is to be expected after this saturation of the rock surface has been reached.

It is thus concluded that if oil migrates for a long distance through porous limestone, the composition of the oil will be

changed considerably, provided no external factors enter in. The limestone traversed will become coated with the heavier oil, and the lighter oil will pass on. The fact that shows and coatings of oil are found in a great many limestones in which no commercial production has been obtained makes probable the belief that much oil has been absorbed on migration through limestone; frequently all the oil in the formation may have been so absorbed, leaving none to collect in a pool. This is not the case with sandstones owing to the low absorptive power of sand.

Since most limestone oils are heavy oils, it must be concluded that they have not migrated over long distances, so that the denser fractions have not been removed, or else that some reactions have taken place within the oil which will cause polymerization or the formation of denser hydrocarbons. The association of limestone oils with sulphur and sulphur compounds leads to the view that with the absorption of these compounds, reactions take place that yield a heavier oil than would be formed in their absence.

As the first experiments performed indicated that not only did heavy oil adhere to the surface of the limestone, but light fractions of the nature of kerosene were absorbed by the rock, it was decided to attempt to find out how much oil was absorbed. These experiments are described below.

### RELATIONS BETWEEN OIL AND WATER IN LIMESTONE.

Several experiments were tried to find out how oil would act in limestone in contact with water.

In the first experiment a glass tube two inches in diameter and one and one half feet long was half filled with limestone crushed and sized between 16 and 32 mesh. This coarse limestone was just covered with water. The remainder of the tube was then filled with limestone crushed and sized smaller than 120 mesh and completely saturated with crude oil having a gravity of 39.8° A.P.I. After two days the oil had moved down into the coarse limestone about three eighths of an inch, and after one month some of it had moved through the water-soaked limestone to the bottom of the tube, though most of that which had moved down

was between 4 and 5 inches below the top of the water-soaked limestone.

The experiment was repeated with various amounts and sizes of limestone fragments and in all cases the oil moved downward into the coarse water-soaked limestone from the finer oil-soaked limestone above it. Migration from the fine limestone into the coarse ceased, however, as soon as enough of the fine limestone was saturated with water to prevent the oil above from coming in contact with the coarse limestone.

In another experiment a fine powder saturated with oil was placed below a coarse limestone saturated with water. Here the water displaced the oil in the fine powder.

Thus water tends to displace oil in a finely porous limestone just as it does in sand,[2] but since the surface tension between oil and limestone is very small, oil may tend to move downward with respect to water when the water has formed a film over limestone, provided there is sufficient room for movement to take place.

In some of these tests voids were noted in the water-soaked limestone. Oil on migrating downward did not fill these voids but passed between them and the limestone.

### MIGRATION OF OIL IN LIMESTONE BY CAPILLARITY.

To find out what effect limestones having various amounts of porosity have on crude oil which passes through them by capillary action, a member of experiments were performed using dolomitic limestone as the porous medium. The limestone was crushed to various sizes, screened, and then packed in glass tubes and allowed to stand upright with the bottoms of the tubes submerged in oil.

The tubes used were about two inches in diameter and, on the average, about 20 inches long. They were plugged at the bottom by corks with grooves cut in the sides to permit oil to enter. The filled tubes were shaken until no further settling of the limestone was observable.

Glass battery jars were used as reservoirs for the oil. To minimize evaporation a cardboard with a hole cut in the center for

[2] *Cf.*, R. Van A. Mills, ECON. GEOL., vol. 15, p. 398, 1920.

the tube was placed on top of the jar and sealed to the jar and to the tube with wax. Another small cardboard was sealed on top of the tube. Pinhole openings were left in both covers.

The oil used in most of the experiments was from the Trenton limestone of Ohio. It had a gravity of 38° to 40° A.P.I. Other oils used were from the Texas Panhandle—gravity 38° A.P.I.

The oil was allowed to pass upward through the powdered limestone by capillary action. When the oil reached the top of the limestone or near the top, the oil-saturated limestone was removed from the tube in three nearly equal parts, each part being placed in a separate container. The limestone in the containers was covered with water and stirred and then allowed to stand for 10 or 12 hours, or until no more oil was observed coming to the surface. The oil and water were poured from the container into a separatory funnel and separated. The oil was then filtered through glass wool to remove the particles of limestone held in suspension.

The results of these experiments have been summarized in Table I.

It was thought that the application of a partial vacuum to the top of the tube might speed up the movement of the oil through the limestone, but such was not the case. This is shown by the results obtained from tube No. 8. Not only was the time excessive but the amount of oil lost was much greater than usual. The excessive loss was due to the increased volatilization that took place when the pressure was reduced, the gaseous hydrocarbons passing off through the suction tube. A partial vacuum of approximately 21 millimeters of mercury was supplied by an aspirator or water suction.

In all the experiments, except No. 9, the limestone-filled tubes were allowed to rest on the bottoms of the reservoirs, the lower parts of the tubes being submerged in about three inches of oil. Due to the differential absorption of the limestone, the lighter hydrocarbons were extracted from the oil but since the tubes were resting on the bottoms of the reservoirs these light oils were removed from a comparatively small portion of the oil, diffusion of the light hydrocarbons downward being very slow.

| A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Vol. Oil at Start in c.c. | Gravity °A.P.I. | Weight. Grams. | Vol. Left in Reservoir. | Gravity °A.P.I. | Weight. | Quantity and Nature of Crushed Limestone in Tube. | Time in Hours. | Volume of Oil Washed Out. | Gravity °A.P.I. | Weight. | Viscosity Water = 1. | Volume of Oil Absorbed and Lost. | Weight in Grams. | Gravity °A.P.I. | Percentage Absorbed and Lost. (N/N−J) × 100. |
| 1 | 2400 | 36.0 | 2016 | 2370 | 36.5 | 2004 | None | 192 | | | | | 21 c.c. | 12 | | |

| A No. | B Vol. Oil at Start in c.c. | C Gravity °A.P.I. | D Weight, Grams. | E Vol. Left in Reservoir. | F Gravity °A.P.I. | G Weight. | H Quantity and Nature of Crushed Limestone in Tube. | I Time in Hours. | J Volume of Oil Washed Out. | K Gravity °A.P.I. | L Weight. | M Viscosity Water = 1. | N Volume of Oil Absorbed and Lost. | O Weight in Grams. | P Gravity °A.P.I. | Q Percentage Absorbed and Lost. (N/N–J) × 100. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2400 | 36.9 | 2016 | 2379 | 36.5 | 2004 | None | 192 | | | | | 21 c.c | 12 | | |
| 4 | 2400 | 39.2 | 1989 | 2210 | 35.9 | 1868 | 19″, 16 to 32 mesh. | 380 | 43 c.c. | 35.0 | 36.5 | 2.99 | 147 | 84 | | 69.6 |
| 5 | 500 | 40.2 | 412 | 165 | 35.9 | 139 | 19″, 60 to 80 mesh. | 169 | *A* 1<br>*B* 26<br>*C* 71 | 35.5<br>36.4<br>36.8 | 0.8<br>21.9<br>59.7 | —<br>2.24<br>2.00 | 237 | 190 | 44.9 | 70.4 |
| 6 | 700 | 37.9*a* | 585 | 335 | 34.7 | 285 | 19″, 60 to 80 mesh. | 647 | *A* 30<br>*B* 44<br>*C* 33 | 33.2<br>34.0<br>34.7 | 25.8<br>37.6<br>28.1 | 4.23<br>3.80<br>3.64 | 258 | 208 | 43.2 | 70.6 |
| 7 | 1500 | 40.2 | 1236 | 1150 | 37.8 | 961 | 20″, 60 to 80 mesh. | 98 | *A* 29<br>*B* 32<br>*C* 56 | 35.9<br>36.3<br>37.9 | 24.5<br>27.0<br>46.8 | 2.10<br>2.21<br>1.93 | Not determined | | | |
| 8 | 3050 | 37.9*a* | 2548 | 1600* | 35.9 | 1352* | 20″, 60 to 80 mesh. | 358 | *A* 35<br>*B* 38<br>*C* 32 | 33.3<br>34.3<br>36.0 | 30.1<br>32.4<br>27.0 | 6.47<br>3.86<br>3.43 | 1345* | 1106 | 40.6 | 92.7* |
| 9 | 3000 | 38.6 | 2496 | 2530 | 36.4 | 2132 | 18″, 60 to 80 mesh. | 244 | *A* 35<br>*B* 43<br>*C* 51 | 36.0<br>36.8<br>37.2 | 29.6<br>36.2<br>42.8 | 2.59<br>2.23<br>2.10 | 341 | 255 | 57.8 | 72.5 |
| 10 | 3200 | 38.6 | 2662 | 2670 | 36.0 | 2256 | 37″ 60 to 80 mesh | 768 | *A* 80<br>*B* 139<br>*C* 58 | 32.7<br>35.4<br>37.2 | 68.9<br>117.8<br>48.7 | 2.81<br>2.53<br>2.11 | 253 | 171 | 77.8 | 47.7 |
| 11 | 1500 | 40.2 | 1236 | 1175 | 35.1 | 997 | 20″, 80 to 120 mesh | 95 | *A* 35<br>*B* 49<br>*C* 64 | 36.6<br>36.9<br>37.1 | 29.5<br>41.2<br>53.4 | 2.29<br>2.08<br>1.88 | Not determined | | | |
| 12 | 2250 | 37.9*a* | 1879 | 1650* | 35.9 | 1395 | 18″, 80 to 120 mesh | 310 | *A* 32<br>*B* 43<br>*C* 40 | 33.7<br>34.7<br>35.4 | 18.8<br>36.6<br>32.9 | 4.34<br>3.16<br>2.10 | 495* | 395 | 45.6 | 82.5* |
| 13 | 3000 | 36.9 | 2521 | 2580 | 36.0 | 2180 | 17″, 120 to 200 mesh | 152 | *A* 93<br>*B* 62<br>*C* 45 | 35.2<br>35.8<br>36.4 | 79.8<br>53.3<br>37.9 | 2.75<br>2.64<br>2.53 | 220 | 170 | 49.6 | 41.9 |
| 14 | 1600 | 40.2 | 1319 | 1400* | 38.0 | 1169 | 17″, quartz sand 60 to 80 mesh | 55 | *A* 49<br>*B* 40<br>*C* 22 | 35.1<br>35.8<br>36.0 | 38.6<br>33.8<br>18.6 | 2.85<br>2.80<br>2.53 | 89* | 59 | 60.7 | 42.5* |
| 15 | 2000 | 40.2 | 1648 | 1790 | 37.1 | 1503 | 18″ argillaceous sand 80 to 160 mesh | 76 | *A* 59<br>*B* 53<br>*C* 55 | 34.6<br>35.2<br>35.8 | 50.2<br>45.0<br>46.5 | 3.76<br>2.19<br>1.91 | 43 | 4(?) | | 20.4 |

* Approximate. *A* Bottom third of tube. *B* Middle third of tube. *C* Top third of tube. *a* Panhandle crude—all others Ohio crude.

Tube No. 9 was placed in the reservoir with the bottom of the tube just below the surface of the oil so as to permit light hydrocarbons to diffuse upward to replace those extracted from the upper portion of the oil. That this did occur and that the limestone extracted lighter hydrocarbons than usual is shown by the fact that both the oil washed out and the oil not recovered were of a higher gravity A.P.I. than the corresponding oils in experiment 5, which was of a similar nature except that the bottom of the tube rested on the bottom of the reservoir.

Some experiments were tried similar to those summarized in the table, in which a heavy asphaltic oil from the Embar limestone of Wyoming having a gravity of about 25° A.P.I. was used. Because of the high viscosity of this oil the amount of upward migration into the limestone was almost negligible.

Two tubes were filled with crushed limestone for the experiments. Both were placed upright in a reservoir of oil. Suction was applied to the top of one tube but not to the other. In the tube without suction, oil migrated up into the limestone about one inch in two weeks. In the other tube the oil did not move through the limestone at all but slipped between the limestone and the surface of the glass tube.

After a tube containing limestone sized smaller than 160 mesh was saturated with oil the reservoir in which it stood was filled with water. After seven weeks the water had risen about eight inches into the limestone, oil rising to the surface of the water. After a year about two thirds of the oil has moved down and out of the bottom of the tube, being displaced by water.

The experiments prove that fractionation of oil does take place when crude oil passes through limestone, since in every case the oil remaining in the reservoir after completion of the experiment had a higher specific gravity than the original crude. That the loss of the light hydrocarbons was not due to evaporation is shown by the results of the blank experiment, No. 1. Fractionation is also shown by the fact that the portions of the oil which moved different distances through the limestone differ from each other in practically all cases in gravity, index of refraction, and viscosity.

Oil is fractionated not only by limestone but also by granite, quartz sand, argillaceous sand, gypsum, and brick dust. This implies that oil might be fractionated by practically any "stony" substance, provided the pore spaces are small. All of these substances however, do not have equal fractionating power.

Because of the comparatively large quantity of absorbed oil which cannot be recovered from the limestone, it is doubtful if limestone can be used as a commercial filter unless some method is devised whereby a large portion of this oil can be extracted.

### FLUSHING EXPERIMENTS.

In order to obtain an estimate of the percentage of oil that might be driven from a saturated limestone reservoir by various solutions, and to determine the relative efficiencies of the solutions, a number of experiments were performed as described below.

*Irregular Introduction of Solutions.*—This experiment was carried out in three glass tubes corked at the bottom and set up vertically. The tubes were about three inches in diameter and about four feet long. Inside each large tube was placed a smaller tube one half inch in diameter. The smaller tube extended from the bottom of the large tube to approximately a foot above the top.

Each large tube was filled with crushed limestone sized between 9 and 80 mesh. The limestone was allowed to stand submerged in oil until it was thoroughly saturated, complete saturation being determined by crushing some of the large fragments and examining them under a microscope.

The oil used to saturate the limestone in each case was from the Trenton limestone of Ohio, and had a gravity of 39.2° A.P.I.

The solutions used for flushing the oil were water, a deci-normal solution of sodium carbonate, and a deci-normal solution of acetic acid. The flushing solutions were poured into the small tubes and came in contact with the oil-saturated limestone at the bottom. They were added in an irregular manner over a period of 48 hours.

The results of the experiment as summarized in Table II in-

dicate that the acetic acid solution is more efficient than either water or the sodium carbonate solution.

TABLE II.

| Tube No. | 1[a] | 2[b] | 3[c] |
|---|---|---|---|
| Vol. oil at start | 1,440 c.c. | 1,314 c.c. | 1,278 c.c. |
| Gravity A. P. I. | 39.2 | 39.2 | 39.2 |
| Vol. sol. added when first sol. came through limestone[d] | 1,140 c.c. | 1,120 c.c. | 1,067 c.c. |
| Vol. oil out when first sol came through limestone[d] | 990 c.c. | 1,015 c.c. | 1,058 c.c. |
| Per cent | 68.7 | 77.2 | 82.8 |
| Total sol. added | 1,240 c.c. | 1,220 c.c. | 1,167 c.c. |
| Total oil recovered | 1,062 c.c. | 1,108 c.c. | 1,086 c.c. |
| Per cent | 73.8 | 84.3 | 84.9 |
| Gravity of recovered oil °A. P. I.[e] | 37.4 | 37.4 | 37.7 |

[a] Water used as flushing solution.

[b] Deci-normal solution of sodium carbonate used as flushing solution.

[c] Deci-normal solution of acetic acid used as flushing solution.

[d] The disparity in these amounts is explained by the fact that some oil was displaced at the bottom of the tube and floated up through the flooding tube. This was subtracted from the volume of the oil originally in the tube and is not included in the table.

[e] Difference in gravity due to absorption of light hydrocarbons by the limestone.

*Continuous Introduction of Solutions.*—The three tubes were again set up, filled with limestone sized between 9 and 80 mesh and saturated with oil as before. In this experiment the flushing solutions, water, a deci-normal solution of sodium carbonate, and a deci-normal solution of acetic acid were introduced continuously into tubes Nos. 1, 2, and 3 respectively, for a period of about ten hours, or until the oil-solution ratio was about one to one hundred.

The results of the entire experiment are summarized in Table III. The curves in Fig. 1 show the relation between the percentage of oil recovered and the time for the first eight-hour period of continuous introduction of solutions.

At the end of the eight-hour period, 100 c.c. of flushing solution was added to the top of each tube and allowed to stand for about 18 hours. At the end of that time 40 c.c. of oil had accumulated at the top of tube No. 1, 109 c.c. at the top of tube No. 2, and 73 c.c. at the top of tube No. 3. This oil was re-

moved, 100 c.c. more solution added to each tube, and allowed to stand for 14 hours. In this time 37 c.c. of oil collected at the

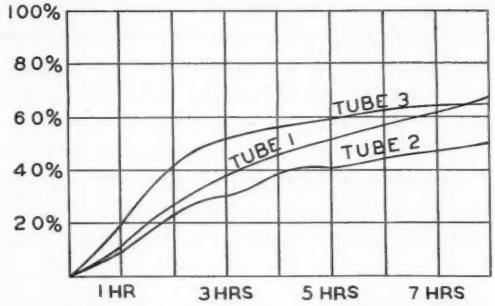


FIG. 1. Relation between percentage of oil recovered and time during which continuous flooding was carried on. Tube 1, water; Tube 2, $Na_2CO_3$ solution; Tube 3, $CH_3COOH$ solution.

TABLE III.

| Tube No. | 1 | 2 | 3 |
|---|---|---|---|
| Vol. oil at start | 1506 c.c. | 1505 c.c. | 1551 c.c. |
| Gravity A. P. I. | 38.6 | 38.6 | 38.6 |
| Flushing solution | Water | N/10 $Na_2CO_3$ | N/10$HC_2H_3O_2$ |
| Vol. oil out when first sol. came through limestone | 871 c.c. | 181 c.c. | 180 c.c. |
| | 57.6% | 12.0% | 11.6% |
| Time in hours | 6 | .5 | .5 |
| Total oil out at end of first run | 1069 c.c. | 850 c.c. | 1069 c.c. |
| | 71.0% | 56.5% | 68.9% |
| Total sol. added at end of first run | 1322 c.c. | 1701 c.c. | 3502 c.c. |
| Total oil out at end of second run | 1109 c.c. | 959 c.c. | 1142 c.c. |
| | 73.6% | 63.7% | 73.6% |
| Total sol. added at end of second run | 1422 c.c. | 1801 c.c. | 3602 c.c. |
| Total oil out at end of third run | 1152 c.c. | 1115 c.c. | 1234 c.c. |
| | 76.5% | 74.0% | 79.5% |
| Total sol. added at end of third run | 1799 c.c. | 3260 c.c. | 5064 c.c. |
| Total oil out at end of fourth run | 1172 c.c. | 1139 c.c. | 1258 c.c. |
| | 77.8% | 75.6% | 81.1% |
| Total sol. added at end of fourth run | 2229 c.c. | 3634 c.c. | 5748 c.c. |
| Total oil out at end of fifth run | 1192 c.c. | 1161 c.c. | 1278 c.c. |
| | 79.1% | 77.1% | 82.3% |
| Total sol. added at end of fifth run | 2868 c.c. | 4193 c.c. | 6353 c.c. |
| Total oil out at end of sixth run | 1198 c.c. | 1165 c.c. | 1282 c.c. |
| | 79.5% | 77.4% | 82.7% |
| Total sol. added at end of sixth run | 2968 c.c. | 4297 c.c. | 6484 c.c. |
| Total oil out at end of seventh run | | 1174 c.c. | 1294 c.c. |
| | | 78.0% | 83.4% |
| Total sol. added at end of seventh run | | 4388 c.c. | 6574 c.c. |

top of tube No. 1, 15 c.c. at the top of No. 2, and 10 c.c. at the top of No. 3. This oil was removed and continuous flushing again begun. In 30 minutes 277 c.c. of water was run through tube No. 1 and six c.c. of oil were recovered; in about two hours 1250 c.c. of sodium carbonate solution was run through No. 2 and 92 c.c. of oil was recovered; in two hours 1172 c.c. of acetic acid solution was run through No. 3 and 46 c.c. of oil recovered. In each case when flushing was discontinued, the ratio of the volume of solution introduced to oil recovered was about one hundred to one. This process was continued for a total of seven days, solutions being introduced at night and the accumulated oil removed the next day.

On the seventh day, the 100 c.c. of water which had been added to tube No. 1 the previous day had disappeared into the limestone. This was probably due to the formation of a gas pocket previous to the introduction of the solution and the later escape of the gas. The formation of the pocket may have been due to vaporization of some of the absorbed oil although this was not noted in any other experiment. It was definitely not due to leakage. On tubes 2 and 3 such a small quantity of oil had accumulated that the experiments were discontinued.

In this experiment the efficiency of the solutions was: (1) acetic acid, (2) water, and (3) sodium carbonate.

On comparing these results with those of the first flushing experiments it will be noted that the average recovery obtained by continuous flooding was 70.3 per cent. of the original volume of oil, whereas by irregular flooding it was 81.0 per cent. After all of the oil that could be collected by continuous flooding was obtained and the tubes were flooded irregularly, the average recovery was 80.3 per cent.

The relative efficiency of the flooding agents used were water 76.7 per cent., sodium carbonate solution 80.9 per cent., and acetic acid solution 83.8 per cent. This should not, however, be considered an absolute index of the value of the solutions, as many other variables must be considered. Of these, the most obvious are the irregular nature of the openings and the probable tendency

to greater ease of channeling in some tubes than in others. Probably the main cause for the greater efficiency of the acetic acid, however, is the formation of carbon dioxide by reaction with the limestone and the consequent introduction of gas. The fact that calcium acetate and sodium carbonate are both basic tends to confirm Nutting's [3] views as to the efficiency of basic solutions in the removal of oil.

*Continuous Introduction of Water into Inclined Tubes.*—The fore-going experiments were all performed with the tubes containing the limestone standing vertically. To approximate natural conditions, a series of seven tubes were filled with limestone and saturated with oil as in the previous experiments, and were inclined at angles of 5°, 10°, 15°, 30°, 45°, 60°, and 75° respectively.

The previous experiments having rather conclusively demonstrated that the amount of oil recovered is largely independent of the flushing solution, the oil was flushed from all these tubes with water.

Although continuous flushing was attempted in these tubes, it was found that it was impossible to introduce measured amounts of water into tube No. 1 as fast as it would pass through the tube. The others were flushed continuously, however, until the water-oil ratio was about one hundred to one, when they were allowed to stand over night. On the three following days the tubes were again flushed until the water-oil ratio was one hundred to one.

The results of the experiment are summarized in Table IV. Fig. 2 represents the relation between percentage of oil recovered and time for the intitial flushing period.

*Continuous Introduction of Water into Inclined Tubes at Controlled Rates.*—Water was introduced into tubes filled with oil soaked limestone, crushed and sized as before, at rates of 400, 200 and 100 c.c. per hour, respectively. These tubes were inclined at an angle of 15°.

Table V shows the results obtained in these experiments to-

[3] Nutting, P. G., Econ. Geol., vol. 23, p. 234, 1928.

TABLE IV.

| Tube. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Inclination in degrees | 5 | 10 | 15 | 30 | 45 | 60 | 75 |
| Vol. of oil at start . . | 1700 c.c. | 1700 c.c. | 1800 c.c. | 1492 c.c. | 1375 c.c. | 1207 c.c. | 968 c.c. |
| Gravity A. P. I. . . . . | 36.9 | 36.9 | 36.9 | 36.9 | 37.2 | 37.2 | 37.2 |
| Vol. oil out when water came through limestone . . . . . | | 91 c.c. 5.3% | 181 c.c. 10.0% | 80 c.c. 5.3% | 629 c.c. 45.6% | 627 c.c. 51.9% | 406 c.c. 41.9% |
| Time in hours . . . . . | | .5 | .5 | 1.5 | 1.0 | 2.0 | 2.0 |
| Total oil out at end of first run . . . . . | 704 c.c. 41.4% | 1016 c.c. 66.2% | 1087 c.c. 60.0% | 524 c.c. 35.0% | 836 c.c. 60.8% | 908 c.c. 74.4% | 734 c.c. 75.6% |
| Total water added at end of first run . . . . | 7514 c.c. | 4106 c.c. | 9756 c.c. | 1453 c.c. | 3168 c.c. | 1894 c.c. | 3089 c.c. |
| Total oil out at end of second run . . . . . | 983 c.c. 63.7% | 1046 c.c. 67.4% | 1197 c.c. 66.5% | 620 c.c. 41.5% | 930 c.c. 67.7% | 1015 c.c. 84.0% | 786 c.c. 81.2% |
| Total water added at end of second run . . | 10386 c.c. | 5257 c.c. | 11341 c.c. | 2162 c.c. | 3745 c.c. | 2171 c.c. | 3468 c.c. |
| Total oil out at end of third run . . . . . | 1066 c.c. 68.6% | 1066 c.c. 68.6% | 1228 c.c. 68.1% | * | 985 c.c. 71.6% | 1042 c.c. 86.3% | 800 c.c. 82.5% |
| Total water added at end of third run . . . | 12328 c.c. | 6333 c.c. | 12049 c.c. | | 4200 c.c. | 2514 c.c. | 3739 c.c. |
| Total oil out at end of fourth run . . . . . | 1072 c.c. 68.9% | 1070 c.c. 68.9% | 1233 c.c. 68.5% | | 1012 c.c. 73.6% | 1051 c.c. 87.0% | 806 c.c. 83.2% |
| Total water added at end of fourth run . . | 12872 c.c. | 6665 c.c. | 12279 c.c. | | 4279 c.c. | 2596 c.c. | 3803 c.c. |

* Discontinued, tube leaking.

gether with the results obtained by flooding a tube that contained limestone which had been thoroughly wetted with water prior to addition of the oil, at the rate of 50 c.c. per hour.

It will be observed that the amount of oil recovered in each of the three cases where Ohio crude of approximately the same gravity and viscosity was used, was practically the same regardless of the rate of flooding. Where Panhandle crude with a high viscosity was used, by-passing of the oil resulted in a recovery of less than a third of that obtained from the Ohio crude. Recovery

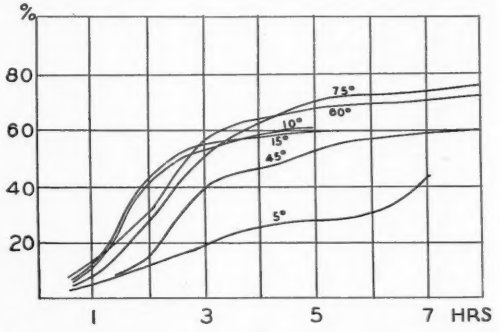


FIG. 2. Relation between percentage recovery and time of continuous flooding with inclined tubes.

from the water-soaked lime was equal to the highest recovery obtained from any experiments.

In every case there was a decrease in the gravity of the oil, indicating absorption of the lighter fractions, and this decrease in each experiment was proportional to the time of contact between the limestone and oil.

The slight loss of gravity in the last experiment indicates the effectiveness of a water film in preventing absorption of oil by limestone.

In comparing the results of the first three experiments in this group, it is found that the total recovery of oil is practically independent of the rate of flooding, although there is undoubtedly

* Discontinued, tube leaking.

an optimum rate which will involve the handling of the smallest possible amount of water From the data available, the slowest rate of production practicable appears to be the most efficient.

TABLE V.

| No. | Vol. of Oil at Start in c.c. | Original Gravity of oil, Degrees A.P.I. | Rate of Flooding c.c./hr. | Elapsed Time in Hours When Water Broke Through. | Total Oil Obtained c.c. | % | Change in Gravity A.P.I. |
|---|---|---|---|---|---|---|---|
| 1 | 1363 (Ohio). | 36.8 | 400 | ¾ | 872 | 64 | 3.0 |
| 2 | 1247 " | 36.8 | 200 | 3 | 791 | 63 | 4.6 |
| 3 | 1187 " | 37.7 | 100 | 2¾ | 801 | 67 | 4.5 |
| 4 | 1157 (Panhandle). | 37.6 | 100 | ¾ | 220 | 19 | 5.2 |
| 5* | 1050 (Ohio) | 36.9 | 50 | 18 | 907 | 86 | 1.2 |

* Limestone wetted with water before introduction of oil.

## CONCLUSIONS.

The experiments described above show that oil will migrate through limestone under the influence of capillarity, but that most of the oil entering the limestone in this way is absorbed by the limestone itself. In migrating from a rock with low permeability to a very porous rock, such as forms the typical limestone reservoir, the oil near the contact is replaced by water until there is a continuous body of water separating the oil from the water-saturated permeable rock. Interchange then ceases.

It is thus entirely probable that limestones do not permit the migration of oil to take place through them unless they have a permeability similar to that of a limestone reservoir.

The lighter fractions of the oil that comes in contact with limestone are absorbed by the limestone. Consequently, the removable oil becomes heavier and, since capillarity is shown to have a greater effect on the light fractions than on the heavier (Cf. Table I.), it follows that oil in a fine grained limestone will tend to become a thick, viscous mass that will effectively prevent any migration taking place. In a thick reservoir such as is encountered in West Texas these heavy residues may collect in tighter

zones within the reservoir with the result that the porous limestone is divided into " pays " separated by an asphaltic limestone, as well as by other impervious beds. Each of these " pays " may contain oil, water, and gas, which differ from the fluids contained in the zones nearby.

This division of a reservoir into zones makes very difficult the application of experimental results to field conditions. Although the experiments described above indicate that the rate of production does not affect the total ultimate production of oil from a well, provided periods of rest sufficient to permit the attaining of equilibrium form a part of the program, and provided also that the effect of gas is disregarded, it can by no means be stated that a lime " pay " will be completely drained by wells because of the impossibility of determining whether those wells have been so spaced as to pierce all the more porous zones in the field. It may, however, be stated that it appears as if normal production methods will remove from the area tributary to any individual well all the oil which that well can be expected to produce, regardless of the rate of production, although too rapid production may necessitate the handling of such large amounts of fluid as to make the well a commercial failure. It appears also as if all the oil recoverable from a limestone reservoir can be recovered by pumping and that any unrecovered oil will be absorbed by the limestone and will therefore be unrecoverable, or else that it will be so mixed with water that it cannot be recovered at a profit. It seems, moreover, as if the amount of oil recovered would be from 67 to 87 per cent. of the oil in the formation and that this maximum figure might even be exceeded in the case of limestones with high permeability or which were saturated with water before the entrance of the oil.

If flooding operations are undertaken, the use of solutions does not appear to give results which warrant the extra expense involved.

The low gravity typical of oils from limestone reservoirs appears to be the result of the absorption of the lighter fractions by the rock, a conclusion that is partly verified by the fact that limestones which are stained by a relatively light oil are found

abundantly in the vicinity of productive reservoirs. The so-called "brown lime" of West Texas has been found to yield oil whenever tests were made with solvents, and since fine grinding was required before the oil could be so removed, it is concluded that the whole formation is saturated with oil. The productive horizons in the lime series of West Texas are in the "white lime" which is relatively unstained.

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# A COLLOIDAL ORIGIN OF SOME OF THE KENNECOTT ORE MINERALS.*

S. G. LASKY.†

## PREFACE.

The unique copper deposits of Kennecott, Alaska, are of more than usual interest to geologists because, first, they consist largely of chalcocite; second, the chalcocite is considered of hypogene origin; and third, they are one of the rare deposits in which natural isometric chalcocite exists.

Since the publication of a paper [1] on these deposits in 1920 by Dr. D. H. McLaughlin and myself, the undersigned, in his capacity as consulting geologist to the Kennecott Copper Corporation, has had the opportunity to continue the study of these unusual deposits throughout their development. During the intervening ten years large suites of specimens have been collected and systematically studied to help elucidate the character of the deposits and their origin. The earlier conclusion that the deposit is hypogene was based on detailed field evidence, chemical consideration, and microscopic examinations. The subsequent work has substantiated this conclusion but, in addition, the use of the polarizing reflecting microscope during the last four or five years has shown conclusively that practically all the Kennecott chalcocite is isotropic and is the isometric or high-temperature form. This subsequent study again raised a question that had intrigued Dr. McLaughlin and myself earlier, namely, the possible colloidal origin of some of the hypogene chalcocite intergrowths. Further search was made over a period of six years for those rare but illuminating specimens that disclose peculiar colloform or cauliflower structures. These were polished and studied to help throw light on this point. Several were found to show not only a pronounced colloform structure but also that single crystal plates of covellite crossed more than one of the colloform bands. This structure is stated by Lindgren [2] to

* Presented before the Society of Economic Geologists at the Charlottesville Meeting, April 27, 1930.

† Introduced by Alan Bateman.

[1] Alan M. Bateman and D. H. McLaughlin, "Geology of the Ore Deposits of Kennecott, Alaska," ECON. GEOL., vol. 15, pp. 1–80, 1920.

[2] Waldemar Lindgren, "Metasomatism." Presidential Address, Geol. Soc. Amer., *Bull. Geol. Soc. Amer.*, vol. 36, pp. 247–261, 1925.

be diagnostic of colloidal ancestry. Before this suggestion could be tested further, however, it became necessary to determine the origin of certain of these intergrowths, and the work then digressed into a study of the mixing and unmixing of these covellite-chalcocite intergrowths. As the covellite of these intergrowths was found to dissolve readily in chalcocite upon application of heat,[3] and to unmix again to form intergrowths, the question was once more raised whether such unmixing in nature may have taken place during a gel stage. At this point Mr. Lasky, who had been in the Engineering and Geologic Departments at Kennecott, began a course of study at Yale in the use of the reflecting microscope, and the specimens and material were turned over to him for one of his problems. The following pages present the results of his study of this question.

ALAN BATEMAN.

## INTRODUCTION.

Ore deposits of copper sulphides that contain isometric, and therefore hypogene, chalcocite are sufficiently rare as to be of unusual geologic interest. The large bodies of chalcocite at Kennecott, Alaska, are of this variety and origin, as was shown by Bateman and McLaughlin[4] in 1920. They concluded that the chalcocite was formed above a temperature of at least 91° C.[5] and pointed out that the limestone and dolomite in which the ore occurs show no alteration and that silicification is entirely lacking. The sulphides occur, even microscopically, in intimate contact with the unaltered limestone.

Colloform structures are present in the Kennecott ores. To account, among other things, for the existence of these colloform structures and the lack of alteration of the limestone, Bateman and McLaughlin[6] suggested a possible colloidal origin for the deposits. Quoting from their paper:

> It would explain (1) the concentration of the copper in the limestone; (2) the lack of silicification or other alteration of the wall rock; (3) the remarkable purity of the ore; (4) the concentric structures which resemble diffusion structures; (5) the combination of open space filling and

[3] Alan Bateman, "Some Covellite-Chalcocite Relationships," ECON. GEOL., vol. 24, pp. 424–439, 1929.

[4] *Op. cit.*

[5] E. Posnjak, E. T. Allen, and H. E. Merwin, "The Sulphides of Copper," ECON. GEOL., vol. 10, pp. 491–535, 1915.

[6] *Op. cit.*, p. 66.

replacement; (6) the inability, displayed by the copper, to migrate far away from the channelways; and (7) the lack of virility of the solutions which prevented them from penetrating through small gouge slips.

During the last few years Lindgren has urged that replacement by colloids [7] is more general than is appreciated by economic geologists. Boydell [8] strongly advocates the influence of colloidal solutions in the formation of mineral deposits. Watanabe [9] has likewise directed considerable attention to the matter. Experimental work has been carried out by others and will be referred to later.

An examination of certain Kennecott specimens, collected by Dr. Bateman specifically to throw light on this problem, was eagerly undertaken by the writer in order to attempt to carry the Kennecott investigation further. The examination was aided by the use of the polarizing reflecting microscope by means of which isometric chalcocite is readily distinguished from the orthorhombic variety. Bateman [10] has described the optical properties of covellite and has noted how, by these properties, covellite is easily distinguished from orthorhombic and isometric chalcocite. The enargite in the ore likewise has distinct optical characteristics which facilitate its recognition. Its "pleochroism" enables it to be distinguished from luzonite.

The instrument that was used to permit the above type of observation, a Leitz Ore Microscope equipped for observation with polarized light, is that used in the Laboratory of Economic Geology, Yale University, and has been described by F. F. Osborne.[11]

[7] W. Lindgren, "Gel Replacement," *Proc. Nat. Acad. Sci.*, vol. 11, no. 1, pp. 5–11, 1925. Metasomatism, *Bull. Geol. Soc. Amer.*, vol. 36, pp. 247–262, 1925.

[8] H. C. Boydell, "The Rôle of Colloidal Solutions in the Formation of Mineral Deposits," *Trans. Inst. Min. and Met.*, 34th Session, 1924. "Operative Causes in Ore Deposition; Ore deposition from colloidal solutions," *Trans. Inst. Min. and Met.*, vol. 37, pp. 98–128, 1928. "A Discussion on Metasomatism and the "Linear Force of Growing Crystals," Econ. Geol., vol. 21, pp. 31–54, 1926.

[9] Manjiro Watanabe, "Some Problems of Diffusion with Special Reference to the Study of Ore Deposits," Sci. Rep. Tohoku. Imp. Univ., Ser. III., vol. 2, nos. 1 and 2, Sendai, Japan, March, 1924.

[10] Alan M.Bateman, "Some Covellite-Chalcocite Relationships," Econ. Geol., vol. 24, pp. 424–439, 1929.

[11] F. F. Osborne, "Technique of Investigation of Iron Ores," Econ. Geol., vol. 23, p. 445, 1928.

ACKNOWLEDGMENTS.

The writer takes this opportunity to acknowledge his indebtedness, especially to Dr. Bateman, who outlined the problem and permitted the use of his mineral collection and with whom various points of the problem were discussed, and whose advice and help in the preparation of this manuscript have been invaluable; and to Dr. M. N. Short of the U. S. Geological Survey, who kindly checked the writer's determination and interpretation of copper-arsenic mineral X and who helped very materially in taking some of the photomicrographs which accompany this paper.

## SUMMARY OF CONCLUSIONS.

The conclusions arrived at in the study of this problem may be summarized briefly as follows: Concurring with Bateman and McLaughlin, it is believed that the ores are mainly of hypogene origin; that they have been transported to their present resting place as highly dispersed colloids, although chemical reaction in electrolytic solutions has probably been a genetic factor, at least in the precipitation of the sulph-arsenides. Much of the covellite is primary. Colloidal diffusion, and unmixing from solid solution with chalcocite,[12] dependent upon the colloidal origin, as well as replacement of the other minerals, have been influential in bringing the covellite into its observed relationships.

## OCCURRENCE OF KENNECOTT ORES.

The geologic setting of the Kennecott ores may be briefly recalled.[13] The country rocks consist of a thick series of lava flows, now altered to greenstone, which are overlain by 3,000 feet of the Chitistone limestone of Triassic age. The lower fifty feet of this formation is limestone, the remainder is dolomitic with variable magnesia content. These rocks dip gently. Some quartz diorite intrusions occur in the general vicinity but are later than the ore.

[12] See "Some Covellite-Chalcocite Relationships," by Alan M. Bateman, *op. cit.*; and a further paper on this subject by Alan M. Bateman and Samuel G. Lasky, in press.

[13] Abstract from Bateman and McLaughlin, *op. cit.*

The rocks are greatly faulted.

The deposits consist of steeply inclined replacement veins and irregular replacement bodies inclosed in the dolomitic limestone. The roots of some of the veins project slightly into the limestone. All the ore is confined to a narrow stratigraphic belt near the base of the Chitistone formation. The veins range in width from a few inches to over 100 feet. In places there may be masses of solid chalcocite from 2 to 80 feet in width and many hundreds of feet in length, the ore from which will run, as mined, from 50 to 75 per cent. copper. The veins pinch to mere cracks at a certain distance horizontally from the underlying greenstone contact, and in their upward extension. Their length along a given level rarely exceeds 800 feet but continuous ore has been followed along the dip of the limestone beds for nearly 4,000 feet.

Massive, hard, brilliant chalcocite is the chief ore mineral. Covellite is fairly abundant. There are present small amounts of enargite, bornite, chalcopyrite, tennanite, and luzonite, whose abundance is in the order named. There is also present a mineral hereafter referred to as "mineral X," which consists only of copper, arsenic, and sulphur but whose etching reactions and optical properties fit neither enargite, luzonite, nor tennantite. It is presumably intermediate in composition between tennantite and enargite and may be a solid solution of those two minerals. A few specimens of pyrite, two of galena, and one of sphalerite have been noted. Some oxidized products, chiefly malachite and azurite, occur scattered throughout the deposits.[14]

Smelter analyses of the ore indicate, in addition to copper, sulphur, silver, and the carbonate radicle, only traces of arsenic, and an iron and silica content that is only a fraction of one per cent. Consequently, the original metallization consisted almost entirely of copper, sulphur, and silver, with minute quantities of iron and arsenic and rare traces of other metals. The ore is thus quite unusual.

[14] For more detailed descriptions of the mineralogy, see Bateman and McLaughlin, *op. cit.*, pp. 35–48.

## PARAGENESIS.

The earliest minerals of the Kennecott ores are contemporaneous chalcopyrite and bornite, which were deposited in widespread, though small quantities, and formed, as it were, the foundation upon which the Kennecott ore bodies were built. This was followed by bornite alone, succeeded in turn by the first tennantite deposition. The second generation of chalcopyrite was then deposited, commonly as rings around the tennantite grains. Probably succeeding the later chalcopyrite, enargite was deposited in the limestone associated with healing solutions that contained calcite. Closely following the deposition of enargite there must have been some vein movement, since much of the enargite is decidedly brecciated and cemented by later minerals. This movement apparently continued slightly into the period of concentric covellite, which came next in abundance. Some of the covellite laths seem to have been bent and show undulatory extinction parallel to the distortion. The delicate adjustment of solutions that is necessary to cause precipitation of arsenious sulphide permitted a certain amount of arsenic to be carried over into this period and small amounts of luzonite, tennantite, and mineral X were formed simultaneously with the covellite, and perhaps some of it slightly later.

The early minerals, chalcopyrite, bornite, tennantite, luzonite, mineral X, and enargite, were deposited in small quantities and somewhat favored the still virgin limestone rather than the already precipitated minerals. There were thus scattered in the limestone veinlets and blebs of many different minerals, together with areas in which later minerals had replaced earlier. The covellite also seemed to favor the limestone areas and replaced pre-existing metallic minerals apparently because replacement of the limestone could not keep pace with the supply of covellite. After the covellite came the chalcocite, almost removing everything in its path either by metasomatic replacement or by solution. In this case, too, the limestone was more easily replaced than the sulphides, so that remnants of each preceding sulphide are still to be found, with here and there original structures still preserved from which it has been attempted to piece together the cycle of events.

COLLOIDAL TRANSPORTATION AND PRECIPITATION OF SULPHIDES.

Clark and Menaul,[15] Lindgren,[16] and Boydell [17] have shown that highly dispersed colloids may penetrate rock openings almost as easily as solutions and may take part in metasomatism. Boydell [18] has suggested a possible mechanism by which an ore of colloidal origin may be formed, and points out that a disperse system may contain within itself [19] most of the factors necessary for precipitation and thus is less dependent upon external causes than are electrolytic solutions. Tolman and Clark [20] and Clark and Menaul [21] have specifically shown that nearly all important sulphides and sulphosalts may become highly dispersed under the influence of $H_2S$, less rapidly by sulphur, in acid, neutral, and especially mildly alkaline solutions. Sodium and potassium salts aid in their dispersion. The colloids may be rapidly precipitated either by loss of the dispersing agent or by coagulating agents such as calcium salts or alumina, *i.e.*, the presence of suitable electrolytes. Mutual reaction between different disperse systems, and also between a precipitate and a disperse phase may also take place, and Boydell [22] also suggests the possible flocculating effect of electrolysis. Calcium carbonate not only acts as an efficient flocculator but it may also undergo replacement by the colloidal sulphides. The precipitate may crystallize rapidly or settle out as a gel through which the electrolytes may diffuse and upon which they may react.

According to Tolman and Clark [23] dispersion of the copper-bearing sulphides takes place in the following decreasing order of readiness: chalcocite (most readily), covellite, bornite, and

[15] J. D. Clark and P. H. Menaul, "Rôle of Colloidal Migration in Ore Deposits," ECON. GEOL., vol. 11, pp. 37–41, 1916.

[16] *Op. cit.*

[17] *Op. cit.*

[18] H. C. Boydell, "Operative Causes of Ore Deposition," *op. cit.* p. 107.

[19] *Idem.*, p. 100.

[20] C. F. Tolman and J. D. Clark, "Copper Sulphides from Colloidal Suspensions," ECON. GEOL., vol. 9, pp. 559–592, 1914.

[21] *Op. cit.*

[22] *Op. cit.*, p. 100.

[23] *Op. cit.*

chalcopyrite. Clark and Menaul [24] found that enargite is much more rapidly dispersed than bornite and only slightly less easily than covellite. Thus the complete order of ease of dispersion would be as follows: chalcocite, covellite, enargite, bornite, chalcopyrite. The order of ease of coagulation, *i.e.*, ease of precipitation, would be the reverse: chalcopyrite, bornite, enargite, covellite, chalcocite. The exact accordance of this order with the order of precipitation of the Kennecott sulphides is striking; the simplified order of precipitation of these sulphides is chalcopyrite + bornite, bornite, sulpharsenides, covellite, chalcocite. The writer wishes to place considerable emphasis upon this agreement since it would be fortuitous indeed if it were accidental.

According to Tolman and Clark,[25] upon coagulation of the dispersed sulphides, the coagulum has a greater tendency to collect upon bornite, if it is present, than upon any other sulphide. This suggests to Boydell an adsorption effect with bornite that may possibly account for its very usual association with, and replacement by, chalcocite in ore deposits. It may also account for the fact that bornite commonly appears to be less resistant to replacement than many of the other sulphides. This is true of the Kennecott ores and is another link in the chain of suggestion of a colloidal origin for these ores (Figs. 1 and 2).

Lindgren [26] states that gels contain absorbed materials as impurities and that in the case of sulphides it is adsorbed sulphur. Thus marcasite is formed by precipitation of colloidal FeS with adsorbed sulphur, which on crystallization unite to form $FeS_2$. The analogy of the composition of marcasite to that of the copper sulphides is clear: chalcocite plus sulphur forms covellite. Also, arsenious sulphide plus sulphur forms arsenic sulphide. The existence of adsorbed sulphur as an impurity is not at all unreasonable. According to Butler and Burbank [27] sulphur tends to exist

[24] *Op. cit.*

[25] *Op. cit.*

[26] W. Lindgren "Metasomatism," *op. cit.*, p. 253.

[27] B. S. Butler and W. S. Burbank, "Relation of Electrode Potentials of Some Elements to Formation of Hypogene Mineral Deposits," A. I. M. E. Tech. Paper 166, Feb., 1929.

in a highly oxidized state before it exists as a sulphide. At an intermediate state it may exist as $S^0$. According to Tolman and Clark [28] carbon dioxide disperses sulphur readily. Sulphur, highly dispersed by the carbon dioxide present in a limestone country such as Kennecott, might thus be co-existent with the colloidal sulphides and might react with them either by adsorption as suggested by Lindgren [29] or by reaction of a disperse system upon an already flocculated precipitate.

If the formulae of the sulphides that have been found at Kennecott are examined, a significant point of similarity immediately presents itself; the chalcocite radical, $Cu_2S$, is common to all of them and therefore must have been present in some form throughout the mineralization period. This is readily in line with the fact that chalcocite is the most difficultly coagulated of the copper sulphides. The formulae may be written as follows: chalcopyrite $= Cu_2S.Fe_2S_3$ (or, admitting the correctness of the formula CuS.FeS, it may be written $Cu_2S.S.2FeS$); bornite $= 2Cu_2S.CuS.FeS$; enargite and luzonite $= 3Cu_2S.As_2S_5$; tennantite $= 4Cu_2S.As_2S_3$; covellite $= Cu_2S.S$. Furthermore, the $As_2S_5$ radical may be written $As_2S_3.2S$.

To review our knowledge to the present point: (1) The order of ease of coagulation of colloidal copper sulphides is exactly the order of precipitation of the Kennecott minerals: (2) chalcocite is the most easily dispersed, therefore the most difficultly precipitated of the sulphides under consideration; (3) it is likewise a necessary constituent of each of them and therefore must have been present throughout the mineralization period; (4) sulphur may occur highly dispersed co-existent with colloidal sulphides with which it may react; (5) in combination with sulphur, chalcocite becomes covellite; and (6) enargite and tennantite are compounds of differing proportions of $Cu_2S$, $As_2S_3$, and S.

In the light of these facts it will be interesting to consider those minerals of the Kennecott series that exhibit colloform structures. Genetically, the chalcopyrite-bornite colloform structures were

[28] *Op. cit.*
[29] *Op. cit.*

the first to be formed. As we have seen, the first sulphide to be precipitated from a disperse series would be chalcopyrite; chalcocite would remain highly dispersed in the electrolyte, which would diffuse through the coagulated chalcopyrite with the following reaction presumably taking place:

$$CuFeS_2 + 2Cu_2S = Cu_5FeS_4,$$

thus forming Liesegang diffusion rings of chalcopyrite and bornite. This follows Ostwald's explanation of the rhythmic arrangement of Liesegang's rings, which is[30] that as the solute diffuses outward from any focus it reacts with the gel to form a third compound which precipitates to form the first ring when the saturation limit is reached; continuous outward diffusion of the soluble salt causes a renewed formation of the third compound in the zone surrounding the first ring until precipitation again ensues, and so on. According to Boydell,[31] however, the most likely explanation of banding is that advanced by Bradford,[32] who considers that rhythmic precipitation is due to "adsorption of the solute in the gel by the precipitate formed," thus impoverishing the gel in the surrounding zone. The net result, at least in the present case, is the same under either explanation.

With the sulph-arsenides the situation is somewhat different. Because of the delicate changes in concentration which determine whether arsenious sulphide is precipitated as a coagulum, comes down as a colloid, or remains in solution, the exact nature of the end products is difficult to estimate. Under certain conditions, diffusion should give rise to the sulph-arsenides in colloform patterns according to the following equation:

$$3Cu_2S + As_2S_3 + S_2 = 3Cu_2S.As_2S_5 = \text{enargite-luzonite}.$$

With but a slow supply of $As_2S_3$ only narrow zones of luzonite would form, the excess sulphur forming covellite with the $Cu_2S$.

[30] A. Knopf, review of "Geologische Diffusionen," by R. E. Liesegang, ECON. GEOL., vol. 8, pp. 803–806, 1913.

[31] "Rôle of Colloidal Solutions, etc.," *op. cit.*, pp. 19 and 20.

[32] S. C. Bradford, *Biochem. Jour.*, vol. 11, p. 14, 1918; vol. 14, pp. 29 and 474, 1920.

On the other hand, slight changes in the character of the solution would cause precipitation and flocculation of $As_2S_3$, uniting with the covellite to form luzonite apparently replacing covellite and in turn being replaced by it.

Some of the arsenic might be expected to be carried over in solution to be later precipitated as a sulph-arsenide later than the covellite.

Tennantite varies in composition from luzonite only in the amount of $Cu_2S$ and S present. Slight changes in solution could therefore cause formation of mineral X, which seems to be a hybrid luzonite-tennantite. With delicate adjustments, perhaps only locally, practically contemporaneous precipitation of chalcocite, covellite, luzonite, and mineral X might ensue with the development of diffusion structures of the four minerals. The confusing arrangements and relationships of the minerals as they exist might in this manner be explained, and all the sulph-arsenides might be relegated to a general age of deposition without any attempt to differentiate.

The chalcocite-covellite colloform structures present a much simpler problem, entailing simply the reaction between chalcocite gel and dispersed sulphur. Whether the copper was transported as colloidal chalcocite with dispersed sulphur as an impurity or as colloidal covellite hardly matters; the net result is the same. Deposition from electrolytic solutions seems to have been confined largely to the sulph-arsenide minerals. It seems more probable that transportation was as chalcocite because of the presence of the chalcocite radical in all the minerals. Furthermore, if the sulphides had a colloidal ancestry, the transporting agent must have been of a dispersing nature, very probably $H_2S$ in solution. $H_2S$ is a reducing agent, and any covellite might be reduced to chalcocite and sulphur. This may be a possible source of some of the adsorbed sulphur that has been postulated.

As the amount of sulphur approached improverishment, chalcocite only would be deposited and would constitute the last mineral of the series.

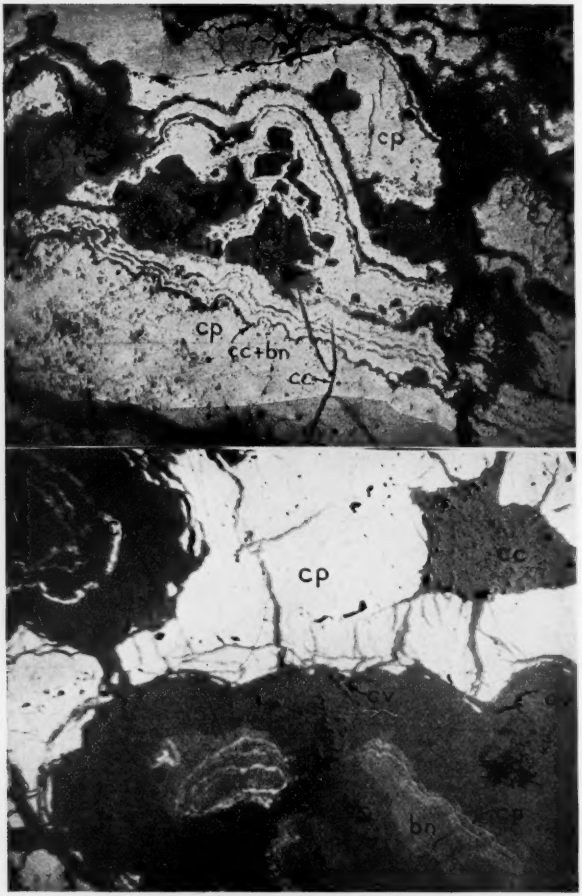


FIG. 1 (above). Bonanza mine. Scalloped bands of chalcopyrite (*cp*) and bornite (*bn*). Much bornite replaced by chalcocite (*cc*), which also veins chalcopyrite. The chalcocite is oxidizing to carbonates (*cb*). ×81.

FIG. 2 (below). Mother Lode mine. Concentric bands of chalcopyrite (*cp*) and bornite (*bn*). Bornite has been replaced by chalcocite (*cc*, dark gray) whereas chalcopyrite has been relatively unattacked, with resulting formation of concentric bands of chalcopyrite and chalcocite, as seen in upper left corner. Chalcocite contains some covellite (*cv*). ×81.

DESCRIPTION AND INTERPRETATION OF COLLOFORM STRUCTURES.

Colloform structures are fairly common as compared to the small quantities in which some of the minerals occur. Alternating scalloped veinlets of bornite and chalcopyrite, with scalloped patterns frequently forming in local development around cores and swellings of bornite, offer a strong resemblance to diffusion structures (Fig. 1). One most interesting specimen exhibits concentric rings of bornite and chalcopyrite so arranged as to resemble the whorls of a fingerprint (Fig. 3).

FIG. 3. Jumbo mine. Complex association of bornite (dark), chalcopyrite (light), and covellite (dark, mottled) in concentric structures. Covellite is largely a replacement of bornite. ×70. After Bateman and McLaughlin, *op. cit.*, Plate VI., c.

Covellite and enargite, covellite and mineral X, and possibly covellite and tennantite are of similar colloform character (Figs. 4 and 5). The covellite in many of the bands or rings is arranged in radiating flakes, pointing toward the center of the diffusion structure; the flakes of covellite cut into and across the bands of the other mineral. Contemporaneous sulph-arsenides—luzonite, mineral X, and tennantite—are found slightly later than this,

FIG. 4 (above). Colloform structures in covellite (*cv*), luzonite (*lz*), and chalcocite (*cc*). Note coarse radial covellite plates and also variable grain size. Two individual crystallization units are represented. Black spots in northeast corner are probably holes formed by shrinkage of the gel during crystallization. × 36.

FIG. 5 (below). Concentric banding in covellite showing different grain in the various bands. The various grain colors of the covellite are due to its strong "pleochroism." The white serrated thread is luzonite. × 81.

sometimes following in tiny threads along the serrated outlines of a covellite band, but most commonly as a replacement of the sulpharsenide ring.

Broad bands of prominently crystalline covellite in chalcocite are of much more common occurrence. The bands are curved, and the broad plates of covellite of which they are formed seem to converge toward a common center.

In many places there is a decided banding in the covellite itself, with some bands formed of coarsely crystalline radiating plates, whereas adjacent bands may be somewhat finer textured (Figs. 4 and 5). A series of concentric bands may be adjacent to a second series concave in a different or opposite direction and apparently representing a separate crystallization unit (Fig. 4). Concentric and radial cracks are common and are usually filled by later material. The concentric cracks are parallel to the banding and in many places follow along the center of the band.

Whenever colloidal ancestry is discussed, the question usually arises as to what are the criteria by which one may recognize such ancestry. There probably are no infallible diagnostic criteria; undoubtedly each case represents an individual problem which must be solved by preponderance of evidence. According to Lindgren [33] the best single indication of colloform ancestry is the presence of what are called "colloform structures." Especially indicative are banding in a mass composed of a single mineral, and the development of concentric and radial cracks. All these are shown by the Kennecott ores.

The colloform structures shown by the Kennecott ores have been described separately but more than one of them may occur in the same microscopic field. The fact that single crystal plates of covellite cross more than one of the colloform bands indicates that these crystals developed later than the banding and thus suggests a colloidal origin. It is true that these traversing crystals may have formed by later replacement, but the manner in which they are intergrown with other crystalline plates of the same band indicates contemporaneous growth. The development of banding

[33] "Metasomatism," *op. cit.*, p. 255.

within the covellite itself is also, according to Lindgren,[34] very suggestive of a colloidal origin.

The occurrence of concentric cracks parallel to the diffusion bands seems decidedly important and suggestive of a previous gel

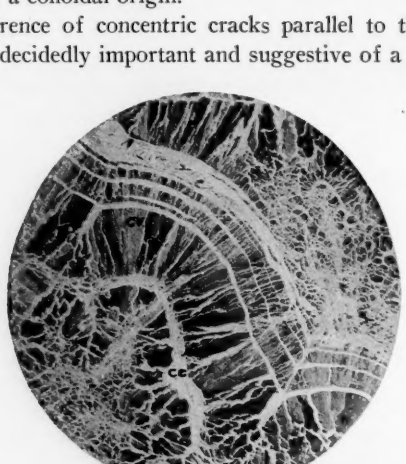


FIG. 6. Bonanza mine. Covellite plates (dark) in radial and scalloped patterns partially replaced by chalcocite (white). ×37. After Bateman and McLaughlin, *op. cit.* (Plate IV., a).

state. Especially so since the radiating crystalline plates that form many of the bands are divergent from the same center around which the banding is formed. Since these three structures have the same center of formation it would seem that they must have developed in response to the same class of laws; *i.e.*, those governing surface tension in a viscous medium, which are those that govern colloidal gels. The presence of adjacent units that have developed around a different center bears out this idea.

The importance of concentric cracks along the central part of some of the bands, with optical continuity of the crystals on either side of the crack, is possibly debatable. The writer thinks that it indicates that cracking, presumably due to concentric shrinkage, took place before complete crystallization of the gel unit, when

[34] *Idem*, p. 255.

the unit was in a state of homogeneous strength throughout. Had cracking taken place after complete crystallization, it probably would have followed the contact, between adjacent bands, which, it seems reasonable to assume, represent the weakest zones within the unit. If cracking did occur before complete crystallization of the mass, as interpreted, it is difficult to avoid the idea of a colloidal ancestry. The optical continuity of the crystalline plates on both sides of the crack can be explained by skeletal growth of the crystals instead of growth by accretion upon a crystalline individual. If a band composed of skeletal crystals were broken apart, the final filling in of the crystals might have the same orientation as otherwise.

There are also other facts that add to the weight of evidence in favor of colloidal ancestry for these ores. Much of the chalcocite is the "steely" variety that on etching gives the "cracked porcelain" pattern, which Lindgren [35] offers as an illustration of colloform grain structure formed by shrinkage during crystallization (Fig. 7).

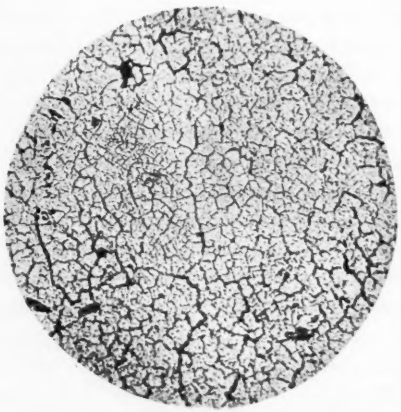

FIG. 7. Bonanza mine. "Steely" chalcocite etched with nitric acid, Cracked porcelain structure, called by Lindgren a colloform grain structure. ×75. After Bateman and McLaughlin *op. cit.* Plate III., b.

[35] W. Lindgren, "Mineral Deposits," 3d ed. p. 948.

Areas that are predominantly fine-grained covellite commonly show a more or less microscopically porous character. The vugs have curved cusp-shaped walls, both convex and concave, and covellite laths extend out from the walls into, and in places across, the vug. Spencer [36] and Bateman [37] suggest high porosity of the metasome as a criterion in favor of colloidal origin. Shrinkage of a gel that had begun to crystallize in fine grains might cause just such openings in the mass in addition to radial and concentric cracks. There is no evidence that the vugs were formed by the leaching out of cores of other material. Conceivably they may be residual spaces left unfilled by mineralization.

### SOLID SOLUTION OF CHALCOCITE AND COVELLITE.[38]

Since the chalcocite is isometric it must contain at least 8 per cent covellite in solution,[39] and at higher temperatures it probably held much more than that. This is the same as saying that even at the point of crystallization of the chalcocite there was still a small amount of adsorbed sulphur and that the resulting covellite below a certain limit controlled by its solubility in chalcocite, did not separate by diffusion. Laboratory experiments [40] show that if the postulated colloidal origin of solid solution is true, unmixing must follow as a natural consequence of slow under-cooling during geologic time.

At many places where chalcocite has penetrated covellite and replaced it, the central part of the chalcocite band is occupied by sharp laths of covellite which in arrangement bear no relation to the invaded material. Presumably, at the elevated temperature at which the chalcocite was deposited, it dissolved the invaded covellite to capacity as it penetrated and filled the openings. Experi-

[36] A. C. Spencer, "Metasomatism and Linear Force of Growing Crystals," Econ. Geol., vol. 21, p. 505, 1926.

[37] Oral communication.

[38] For a more detailed discussion of this subject see Bateman, Alan M., "Some Covellite-Chalcocite Relationships," *op. cit.* and a further paper on this subject by Alan M. Bateman and Samuel G. Lasky in process of publication.

[39] Posnjak, Allen, and Merwin, *op. cit.*

[40] *Idem.* Also "Some Covellite-Chalcocite Relationships" *op. cit.*

ments have amply demonstrated that covellite can be dissolved readily and that the same covellite can be brought out of solution just as readily.[41] Available evidence points to a colloidal origin for the minerals. If this colloidal origin is accepted, solution and ex-solution must also be accepted.

## SUMMARY.

There are a considerable number of readily observable facts about the Kennecott ore minerals that point toward a colloidal origin for these deposits. Some of the facts are very suggestive in themselves, and the aggregate weight seems to be strongly in favor of such ancestry.

Colloform structures are clearly present and in significant relationships. The significance of these structures is upheld by the chemical relationships of the different minerals. A certain order of deposition for colloidal copper sulphides has been experimentally determined[42] and this order is practically paralleled by the paragenesis of the Kennecott sulphides. The presence of the chalcocite radical in the formulae of all the ore sulphides, and the great probability of colloidal sulphur co-existent with highly dispersed sulphides, support a colloidal interpretation.

Some of the sulph-arsenides were clearly deposited from electrolytic solutions. This is explained by the delicate equilibrium which determines the soluble or insoluble condition of arsenious sulphide.

The chalcocite of the ore is the isometric variety and therefore was deposited at a temperature above 91° and must contain a certain amount of covellite in solution. It was the last mineral to be deposited. It has been experimentally demonstrated[43] that covellite is readily soluble in chalcocite at a temperature perhaps as much as 20° below the minimum temperature—91°—which must have existed, and that under-cooling over an extremely short period of time suffices to cause unmixing. Chalcocite and

[41] Work in process of publication.

[42] Tolman and Clark, *op. cit.* Clark and Menaul, *op. cit.*

[43] "Some Covellite-Chalcocite Relationships," *op. cit.*, and a further paper by Alan M. Bateman and Samuel G. Lasky, in process of publication.

covellite must have been in solid solution at the time of deposition; chalcocite apparently also had opportunity to dissolve already precipitated covellite, and unmixing of any excess covellite must have taken place subsequently.

Upon these known facts concerning the Kennecott ores as a foundation, an hypothesis is built that attempts to strike a balance between these three modes of origin: colloidal transportation and replacement; unmixing from solid solutions; and deposition and replacement from electrolytic solutions.

## CONCLUSION.

The sulphides that go to make up the Kennecott ore bodies were transported in a highly dispersed condition and were flocculated upon reaching such an ideal flocculating agent as the limestone. The alumina along thin gouge seams also served to flocculate the sulphides as well as to dam back the solutions.

Chalcocite and sulphur were always present; in the initial stages iron-bearing sulphides, and later arsenic-bearing sulphides, were in predominant though still small amounts. Chalcopyrite, as the most difficultly dispersed and therefore the most readily coagulated, was the first to be precipitated; it reacted with the still dispersed chalcocite to form bornite, and characteristic diffusion structures developed upon crystallization. In like manner followed the precipitation of sulph-arsenides, covellite, and chalcocite, and the development of other coloform structures. The chalcocite, being the most readily dispersed, was the last sulphide to be precipitated with its own identity. It was, however, always present and combined with the other component sulphides as they were coagulated, to form the stable minerals. The sulph-arsenides, however, in part owe their existence to precipitation from solution. Upon crystallization of early coagulated minerals, shrinkage cracks opened in a colloform arrangement—a system of radial and concentric cracks—and these cracks were filled with later coagulated material, with some replacement by the invading material. The covellite, because of the platy, elongate nature of its crystallization, was the most readily and typically cracked.

The chalcocite, in addition to the covellite that it was able to dissolve from the surrounding material by virtue of the high temperature, contained in solution also a certain amount of covellite formed by reaction with the excess sulphur, which at this stage was present in relatively small amount. Upon lowering of the temperature, the covellite tended to unmix and did so in part until equilibrium was reached. The equilibrium point apparently lies above 8 per cent. CuS.

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# A NEW LOCALITY OF GAY-LUSSITE IN EASTERN MONGOLIA WITH ASSOCIATED NATURAL SODA.

K. NIINOMY.

*Introduction.*—The mineral Gay-Lussite ($Na_2CO_3.CaCO_3.5H_2O$) was first described by Boussingault from Venezuela in 1826. Since then it has been noted by Blake from Nevada in 1866, by Pratt from California in 1896 and by Farrington from Wyoming in 1900.

The present paper deals with a new occurrence of Gay-Lussite from Lake Taboos-nor on the eastern edge of the Great Khing-an mountains in eastern Mongolia. The exact location of the lake is 355 km. north of Mukden, in Long. 123° 34′ 1/5–42′ E., and Lat. 44° 44′ 3/5–50′ ½N., and its political location is in Chichang prefecture, Kirin province, Manchuria.

*Topography.*—Lake Taboos-nor ("Salt lake" in Mongolian) which is roughly elliptical in outline and has an average diameter of about 8 km., lies in a flat dry plain—a typical steppe—a part of the eastern Gobi desert, surrounded by many small sand dunes. This plain, which contains the deposits of natural soda, is in the old valley of the Liao, which forms a natural boundary between eastern Mongolia and Manchuria.

The banks of the lake are about 20 meters high, and 25 km. long, some three quarters of this distance being a steep slope showing 11 beds of fine yellowish sandy clay. The remainder is covered by sand dunes. The lake bottom is flat, but near the center there are a number of small mud volcanoes, some of which are one meter high, with a diameter of 10 meters at the base. They have been built up by springs during the dry season. When there is sufficient rainfall in summer, Lake Taboos-nor has some water, but at other times it is almost dry, although the mud volcanoes, which are fed by springs of shallow origin, are moist at all times.

The writer believes that the number of spring outlets was originally small, but that as wind-blown sand accumulated over the lake bed, the number of outlets sought by the water has increased, and at present they are estimated at from 100 to 400 per square kilometer. At one locality near the east-central part of the lake, 1,300 mud volcanoes were counted in an area 100 meters square.

It is not thought that this lake is of the talas type, common in western Mongolia,[1] but that it occupies a depression caused by crustal movements.

*Occurrence of Sodium Minerals.*—The writer first visited the district for two days in January, 1928, in company with Prof. Y. Hattori of the Teachers' College at Mukden and Mr. I. Okada of Tokyo Imperial University. A second visit was made in March, again with Prof. Hattori. At these times the lake was almost dry, and its bed was partially frozen. It was noticed that about one half of the surface of the lake bed was covered by a deposit of thermonatrite ($Na_2CO_3.H_2O$) over 1 cm. thick. In the mud below the surface there were found many small platy crystals of natron ($Na_2CO_3.10H_2O$), which extended to a depth of about 30 cm. Near the surface these at times formed as much as 30 per cent. of the sediment by weight. Below the natron zone was one containing crystals of Gay-Lussite, the identity of which was not at first suspected.

*Occurrence of Gay-Lussite.*—At a depth of 30 cm. below the lake bed, the Gay-Lussite crystals formed about 15 per cent. of the mud by weight; at 60 to 100 cm. depth, 26–28 per cent., below which the amount of the crystals dropped off rapidly to a depth of 200 cm., beyond which depth none were found except at one point 230 cm. deep.

The nature of the mud in which the Gay-Lussite occurs appears to have nothing to do with its distribution, as it is uniform in horizontal and vertical extent.

*Nature of the Mud.*—The sediment in which the Gay-Lussite occurs is a dark gray mud, a sample taken from depth of 90 cm.

[1] Berkey, C. P., and Morris, F. K., "Geology of Mongolia," pp. 306–309, 1927.

and examined by Prof. Hattori, giving the following test for fineness:

| | |
|---|---|
| Particles under .008 mm. diameter | 27 per cent. |
| Particles .008 mm. to .036 mm. | 21 per cent. |
| Particles over .036 mm. | 52 per cent. |

K. Nishida of the Central Laboratory, South Manchurian Railway at Dairen obtained the following results on this material:

| | Per Cent. |
|---|---|
| Gay-Lussite | 25.8 |
| Soluble in water | 64.63 |
| Insoluble in water | 35.37 |
| Insoluble in HCl | .90 |

A complete analysis follows:

| | | | |
|---|---|---|---|
| $SiO_2$ | 37.78 | $SO_3$ | — |
| $Al_2O_3$ | 4.97 | $CO_2$ | 10.32 |
| $Fe_2O_3$ | 1.92 | Cl | Tr. |
| CaO | 6.70 | $H_2O$ | 21.77 |
| MgO | 2.05 | Undet. | 7.35 |
| $Na_2O$ | 7.14 | | |
| | | | 100.00 |

The two following analyses represent I. Gay-Lussite from Lake Taboos-nor, I. Okada, analyst, and II. Theoretic composition of this mineral as given by Dana:

| | I | II |
|---|---|---|
| Insol. HCl | .16 | |
| $SiO_2$ | .08 | |
| $Al_2O_3$ | .00 | |
| $Fe_2O_3$ | .03 | |
| CaO | 19.02 | 18.93 |
| MgO | .01 | |
| MnO | .009 + | |
| $Na_2O$ | 20.40 | 20.93 |
| $K_2O$ | .00 | |
| $CO_2$ | 30.02 | 29.72 |
| $H_2O$ | 30.47 | 30.42 |
| Cl | .00 | |
| $SO_3$ | .00 | |
| | 100.199 | 100.00 |

The Gay-Lussite crystals are transparent, colorless, and short, stout columnar and monoclinic. Some of them are 1 mm. long, but in general they are less than this.

The most common faces determined by Okada were b(010), m(110), c(001), r(112) and e(011).

The specific gravity at 20° C. was 1.991, which is higher than figures given by Dana, his ranging from 1.93–1.95. Okada explains this difference on the ground that the Mongolian crystals are free from cavities, while most of the others described contain small needle shaped ones. The other properties such as conchoidal fracture, glassy luster, brittleness, and hardness, are all normal.

Okada determined the crystals to be optical negative with indices at 20° C. as follows:

$$\alpha D = 1.444 \pm .001$$
$$\beta D = 1.516 \pm .001$$
$$\gamma D = 1.523 \pm .001$$
$$2E_D = 51° 32'$$
$$2V_D = 33° 20'$$

Gay-Lussite easily becomes white and translucent when exposed to the air, even at a temperature of 30° C.,[2] and is partially soluble in cold water. This may explain the rarity of its occurrence For preservation the crystals should be kept in absolute alcohol in a cool room.

*Origin of soda minerals.*—Y. Okamura[3] suggested that the sodium carbonate was brought into the lake by spring waters which rise in the bed, but chemical tests of four spring waters by the writer and his party showed considerable NaCl, and a little $CaSO_4$ and $CaCO_3$ but no free $Na_2CO_3$ or $NaHCO_3$.

A second theory is that the soda was brought in by surface streams, but there is little evidence of former surficial drainage and none exists now. The writer is not prepared to formulate a definite theory at present, but makes the following suggestions.

[2] Wegscheider, R., *Ann. de Chem.* (Liebig), 351, pp. 87–99, 1908.

[3] Jap. Geol. Surv. Bull., "Minerals in Eastern Mongolia," pp. 29–33, 1917.

It is thought the natural soda was probably formed by chemical reactions between such materials as NaCl, $CaCO_3$, and $CO_2$ That first there was formed at depth Gay-Lussite as a result of double decomposition of NaCl and $CaCO_3$ in the mud. This changed to natron at a shallower depth, due to physical and chemical conditions not clearly understood. The natron when exposed on the surface loses some of its combined water and changes to thermonatrite. It is this final product, usually called natural soda, which forms an abundant efflorescence on the lake bed.

The exposure of the natron on the surface is due in part at least to wind erosion during the dry season. The writer does not believe that the thermonatrite has come from urao (trona) as suggested by some.[4]

The chemical processes representing these changes may be somewhat as follows:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2,$$

$$2NaCl + Ca(HCO_3)_2 = 2NaHCO_3 + CaCl_2,$$

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

These reactions are not new, having been stated by a number of investigators.[5] The sodium chloride is believed to have come from connate water contained in the marine sediments of this region.[6]

A second source might be the saline and carbonate springs which are sometimes common in the granite area of the Great Khing-an. Calcium carbonate might also be derived from calcareous parts of organisms contained in the underlying marine

[4] Ikebe, S., Central. Lab. Bull., 1, pp. 1–6, 1910.

[5] Berthollet, C. L., *Jour. Phys. Chim. et d'Hist. Nat.*, vol. 51, pp. 1–9, 1800; Hunt, T. S., *Amer. Jour. Sci.*, (2), vol. 28, pp. 170–187 and 365–383, 1859; Nicholson, E., *Chem. News*, vol. 26, pp. 197–199, 1872; vonKvassay, E., *Jahrb. k.k. geol. Reichsanstalt*, vol. 26, pp. 427–446, 1876; de Mondésir, P., *Compt. Rend.*, vol. 106, pp. 459–562, 1888; Gedroiz, K. K., *Internat. Soc. Soil Science*, 1926, pp. 208–223.

[6] Grabau, A. W., "Stratigraphy of China," Pt. I, 1923, pp. 221–234, 339–340, and 498–504.

formations. The carbon dioxide might be derived from several sources.

In view of the fact that the sodium salts found in the bed of Lake Taboos-nor show a distinct and individually restricted zonal distribution, it seems to the writer that there is more or less genetic relationship between them.

The quantity of the combined sodium salts is undoubtedly large, and may equal a million tons.

The writer wishes to acknowledge the assistance which he has received from Prof. Y. Hattori, Mukden Teachers College, and Mr. I. Okada, of the Tokyo Imperial University.

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# DISCUSSION AND COMMUNICATIONS

## *A QUALITATIVE AND QUANTITATIVE DETERMINATION OF THE ORES OF COBALT, ONTARIO.*

*Sir:* I have read with interest the article that appeared under this title by Professor Ellis Thomson in this journal, volume 25, No. 5, pp. 470–505 and No. 6, pp. 627–652.

Cobalt, Ontario, has long been the classic North American locality for the arsenides of cobalt, nickel and iron. The most abundant of these are arsenopyrite, löllingite, niccolite, smaltite, chloanthite, cobaltite, and gersdorffite. All are hard, and all except niccolite are white and "present more points of similarity than of difference." These hard arsenides are intimately associated with native silver, and metallic cobalt and nickel have been obtained as by-products in the treatment of the silver ores of that locality. For many years it has been generally assumed that smaltite was the principal cobalt mineral in these ores; in fact so prevalent is this belief that text books in mineralogy have stated that smaltite is the most abundant cobalt mineral in nature. This belief is due to the fact that almost without exception the published descriptions of the ores of Cobalt extending from the first systematic microscopic study by Campbell and Knight in 1906 to the present have given the stellar rôle of the hard arsenide minerals to smaltite.

The painstaking and thorough investigation of Thomson has removed the cumulative errors of the past. He has taken unusual care to base his mineral determinations on analyzed material. Many experiments performed on a type suite of analyzed minerals resulted in the use of some eight or ten new etching reagents by which he was able to determine with certainty the different minrals of his reference suite. He then studied microscopically an unusually large suite of specimens from the three principal operat-

ing mines at Cobalt. This study revealed the fact that cobaltite is the most important ore of Cobalt and that it is followed in importance by safflorite, orthorhombic $CoAs_2$, a mineral not hitherto reported from the district. Smaltite, the isometric form of $CoAs_2$, instead of being the most important cobalt-bearing mineral is comparatively rare and unimportant. A series of excellent microphotographs which accompany the article led the reviewer to compare them with previous articles, and he is convinced that in the great majority of cases where smaltite was described and pictured, the mineral was actually cobaltite. The latter mineral usually has a light coppery tinge in reflected light but where it contains an appreciable proportion of iron, the coppery tinge is missing and the mineral has the usual gray color of the other arsenides mentioned.

The term "microchemical test" is one that has caused a great deal of confusion where applied to the study of polished ore minerals. As originally employed by Behrens,[1] the term implies chemical tests for the qualitative determination of elements, usually performed on a glass slide and studied microscopically. This usage has been followed by all European chemists and geologists but in America has been employed only by chemists. When the microscopic study of polished surfaces of ores by reflected light came into general use, the minerals were determined chiefly by their reactions or lack of reactions when subjected to etching by a series of chemical reagents. This etching may bring out internal structure in a mineral, as when chalcocite is etched with nitric acid, but such etching seldom gives any clue as to the chemical elements in the mineral. Following Graton and Murdoch,[2] American investigators have termed these etching reactions "microchemical tests." This usage leads to confusion, and in the text books of Schneiderhöhn and of Van der Veen, etch reactions are referred to as such, retaining for the term "microchemical test" its original meaning. The texts of Murdoch and of Davy-Farnham follow the terminology of Graton and Murdoch, and

[1] Behrens, H., "Mikrochemische Methoden," Amsterdam, 1882.

[2] Graton, L. C., and Murdoch, Joseph, "The Sulphide Ores of Copper," *Trans. A. I. M. E.*, vol. 45, p. 34, 1913.

American and Canadian geologists almost without exception have followed their lead.

Nowhere is this confusion more manifest than in the paper of Thomson. For instance: "These sections were determined partly with the aid of the new microchemical reagents previously mentioned and partly by means of physical tests, confirmation as to the metal content of each mineral being obtained from the familiar ferrocyanide, dimethyl-glyoxime and alpha-nitroso-beta-naphthol tests for iron, nickel, and cobalt respectively. Microchemical tests for copper, lead, and antimony were also used where less common minerals were encountered." From the context one gathers that the "microchemical reagents" of the first sentence of the above quotation refer to the new etch liquids used by the author, whereas the "microchemical tests" of the last sentence refer to qualitative tests for elements. To the reviewer it seems that the European usage is greatly superior.

Foot-note references in Thomson's paper would be more valuable if the dates of publication of the respective papers had been given. In some of them this has been done but in most of them it is omitted. It is of decided interest to the reader whether A's paper was published before or after B's paper on the same subject.

It has long been customary to label the various minerals shown in a microphotograph by suitable abbreviations rather than to print out the entire name on the picture. In doing so there has been a considerable degree of uniformity, the great majority of writers following the abbreviations used by Graton and Murdoch in the paper already cited. Dr. Thomson, however, prefers to devise his own system. The following list compares the usual abbreviations with those of Thomson:

| Mineral. | Usual Abbreviation. | Thomson's Abbreviation. |
|---|---|---|
| Pyrite | py | py |
| Chalcopyrite | cp | ch |
| Galena | gn | ga |
| Sphalerite | sl | sp |
| Pyrrhotite | po | pr |
| Silver | ag | si |
| Niccolite | — | ni |
| Bismuth | bi | bi |
| Bismuthinite | — | bnt |
| Argentite | arg | a |

It would be better if all investigators used the same abbreviations. The most obvious ones for native elements are the chemical symbols for those elements. The abbreviation *si* used by Thomson for silver may easily lead a casual reader to confuse it with silicon.

It has long been known that smaltite, whose formula is usually given as $CoAs_2$, is not a mineral with a definite formula, such as cobaltite, for instance. Not only is the cobalt isomorphous with nickel and iron, but the arsenic varies widely from the theoretical proportion called for by the above formula. On the other hand skutterudite, $CoAs_3$, has a definite formula, as shown by analyses of all specimens from the type locality, Skutterud, Norway. Skutterudite is isometric and almost indistinguishable from smaltite. As the average percentage of arsenic in all the published analyses of smaltite falls between the theoretical percentage called for by the formula $CoAs_2$, and that of skutterudite, Walker concludes that the so-called smaltite consists of isomorphous intergrowths of smaltite and skutterudite.[3] The specimens from Cobalt, Ont., when etched with $HNO_3$ show banding parallel to the outside edges of the crystal. Walker and Thomson both believe that these bands are alternate shells of smaltite and skutterudite.

The reviewer, led by Walker's article, has recently attempted to determine whether these composite crystals were mechanical intergrowths or whether they were homogeneous. Three new analyses of smaltite were made in the chemical laboratory of the U. S. Geological Survey at the request of the present writer. The material was all previously examined microscopically and found homogeneous. The results of the analyses are as follows:

ANALYSES OF SMALTITE (NEW).

| | As | S | Co | Ni | Fe | Cu | Bi | Ins | Total |
|---|---|---|---|---|---|---|---|---|---|
| I..... | 75.4 | 0 | 4.5 | 15.2 | 3.5 | 0.7 | 0 | 0 | 99.3 |
| II..... | 75.3 | – | 10.98 | 5.14 | 5.82 | – | – | 1.44 | 98.68 |
| III.... | 63.42 | 0 | 15.83 | 15.07 | 3.69 | – | 0.86 | 0.32 | 99.19 |

I. Schneeberg, Germany. J. G. Fairchild, Analyst.
II. Horace Porter mine, Gunnison Co., Colo. J. G. Fairchild, Analyst.
III. Schneeberg, Germany. J. J. Fahey, Analyst.

[3] Walker, T. L., "Skutterudite from Cobalt, Ontario," *Amer. Mineralogist*, vol. 6, pp. 54–56, 1921.

In analysis I. the molecular ratio As/Ni, Co, Fe is approximately 2.5 hence the formula approximates $(Co, Ni, Fe)_2As_5$, or for the purpose of comparison it may be expressed $(Co, Ni, Fe)As_{2.5}$. In analysis II. the corresponding molecular ratio is 2.6 and the formula can be expressed $(Co, Ni, Fe)As_{2.6}$. In formula III. the molecular ratio is 1.5 and the corresponding formula $(Co, Ni, Fe)As_{1.5}$.

If smaltite consists of an intergrowth of $CoAs_2$ and $CoAs_3$ as believed by Walker and Thomson, the molecular ratio should never fall below 2.0. Is it possible that the so-called smaltite consists of an intergrowth either mechanical or in solid solution of skutterudite and some end-member with a proportion of arsenic lower than the theoretical $CoAs_2$, say an isometric CoAs? An inspection of the 55 analyses listed in Hintze's Handbuch der Mineralogie shows that 12 of them have percentages of arsenic well below 70. (The theoretical percentage of arsenic in $CoAs_2$ is 71.8).

Let us consider analysis XV., which has the second lowest percentage of arsenic of any in Hintze's list. The specimen is likewise from Schneeberg.

ANALYSIS OF SMALITITE. (From Hintze's Handbuch der Mineralogie.)

| | Percentage. | Ratio. | |
|---|---|---|---|
| As | 58.71 | .783 | .870 |
| S | 2.80 | .087 | |
| Co | 3.01 | .051 | .661 |
| Ni | 35.00 | .596 | |
| Fe | 0.80 | .014 | |
| | 100.32 | | |

The molecular ratio is $.870/.661 = 1.3$ and the formula can be expressed $(Ni, Co, Fe)As_{1.3}$. This suggests that the end members of the isomorphous series smaltite-chloanthite are skutterudite and an unknown isometric mineral (Co, Ni, Fe)As. It is undoubtedly true that the majority of smaltite-chloanthite analyses show a composition between that of theoretical smaltite and skutterudite. The reviewer averaged 58 analyses comprising the

55 of Hintze to which were added the three above given. The result is: As 71.4, S 1.1, Co 9.1, Ni 11.7, Fe 5.0, Total 98.3. This average yields the molecular ratio As, S/Co, Ni, Fe = 2.2.

Does the concentric shell structure brought out by etching smaltite specimens from Cobalt consist of alternate shells of smaltite and skutterudite as believed by Walker and Thomson? The reviewer has a contrary opinion. Of the three specimens of smaltite examined by him, analyses of which are given above, III. showed a concentric shell structure when etched by 1 : 1 $HNO_3$, but I. and II. failed to show it. A specimen of skutterudite from the type locality, whose analysis as already stated corresponds closely to the theoretical formula (Co, Fe, Ni)$As_3$, showed pronounced banding when etched. If the individual shells are of different composition, the difference must be very small. The same reasoning applies to cobaltite from the Columbus mine, Cobalt, Ontario, whose composition as shown by microchemical tests is apparently entirely free from nickel and low in iron. When etched with $HNO_3$ it yields parallel concentric bands.

The reviewer believes that the intergrowths which constitute the so-called smaltite are molecular rather than mechanical.

The reviewer uses the following methods for the determination of the hard arsenides. First by means of polarized reflected light, the minerals are divided into two classes, isotropic and anisotropic. These two classes are about equal in the number of minerals comprising them. Second, by means of etch tests, using the reagents of Davy-Farnham, *i.e.*, 1 : 1 $HNO_3$, 1 : 1 HCl, 20 per cent. KCN, 20 per cent. $FeCl_3$, the minerals are further subdivided into groups. It is found that all the minerals of the smaltite family, including smaltite, chloanthite, and skutterudite give the same etch reactions. These are as follows: $HNO_3$—effervesces; surface stains brown to iridescent, HCl—negative, KCN—negative, $FeCl_3$—stains brown. None of the other hard arsenides gives the above reactions. Finally the relative proportions of cobalt, nickel and iron are estimated by a microchemical test. Material is obtained from a polished section by scraping the surface with a No. 6 Sharps needle. A flat surface is ground on one end of the

needle by holding it against a carborundum wheel. The axis of the needle should make an angle of about 70° with the surface of the wheel.[4] The mineral is harder than the needle, but powder is readily obtained by working the needle back and forth, by which a small crater-like cavity is formed on the surface. It is best to begin working the needle in a crack or pit. The powder is transferred to a glass slide by means of a moist sharpened match or splinter of soft wood. The powder sticks to the wood, being held by capillary attraction. A drop of 1 : 1 nitric acid about 1.5 mm. diameter is placed on a glass slide. The match with adhering powder is brought to the drop, and on touching it, the powder falls into the drop. The amount of powder required is usually about that obtained from a crater-like cavity on the polished surface of approximately 0.20 mm. diameter. The drop is then evaporated to dryness over a small alcohol lamp. Two or three additional drops of $HNO_3$ are successively applied to the residue and each evaporated to dryness. The residue is leached with a drop of 1 : 7 $HNO_3$ and the drop transferred to another place on the slide by means of a capillary pipette. Into this drop is merged a drop of a 3 per cent. solution of potassium mercuric thiocyanate. The cobalt is precipitated out of solution as deep blue spherulites and prisms, the nickel is precipitated as light brown spherulites, and the iron does not precipitate but stains the solution red. As the nickel and cobalt do not form an isomorphous precipitate with the reagent but form separate precipitates widely different in appearance, one can estimate with a surprising degree of accuracy the relative proportions of nickel and cobalt present. The intensity of the red stain imparted by iron is a rough measure of the proportion of that element in the solution. Potassium mercuric thiocyanate is not available in the market but can be made according to directions given by Chamot.[5]

The above procedure does not avail to distinguish between arsenopyrite, FeAsS and löllingite, $FeAs_2$, both of which give the same etch tests with the Davy-Farnham reagents and both of

[4] Short, M. N., and Shannon, E. V., "Violarite and Other Rare Nickel Sulphides," *Amer. Mineralogist*, vol. 15, No. 1, page 6, 1930.

[5] Chamot, E. M., "Elementary Chemical Microscopy," p, 450, New York, 1921.

which contain iron and arsenic. A microchemical test for sulphur will allow such a distinction to be made, but the simple etch test proposed by Thomson is quicker and more convenient. A saturated solution of $FeCl_3$ stains löllingite but is without effect on arsenopyrite.

In conclusion, Dr. Thomson has added another to a valuable series of contributions on Canadian mineralogy.

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## *NOTES ON THE GEOLOGICAL ACTIVITIES IN POLAND.*

*Sir:* I append herewith some notes in regard to the geological work in Poland, which may be of interest to some of your readers.

The Geological Survey of Poland (Service Geologique de Pologne) J. Morozewicz, Director, is naturally the headquarters of geological work. As for economic geology, there is a substation in Borysław, in charge of K. Tołwinski, which is situated in a petroleum district. The second section is in the coal district of Dąbrowa Gornicza, with St. Czarnocki in charge.

Geological investigations are also undertaken by the mining school, by the University at Cracow, and by the Technical High School and the University in Lwów.

The Polish geologists are organized in the Polish Geological Society, which at intervals holds scientific sessions and excursions. Another institution is the Association for the Advancement of Carpathian Geology. These societies and institutions work in many directions.

Among the important mineral resources in Poland are coal, lignite and peat; petroleum gas, or ozokerite, asphalt and bituminous shale; ores of iron, zinc and lead; rock salt, potassium salts, phosphates, clays, and mineral waters. An important part of the geological investigations also is the providing of rock material for streets and railroads.

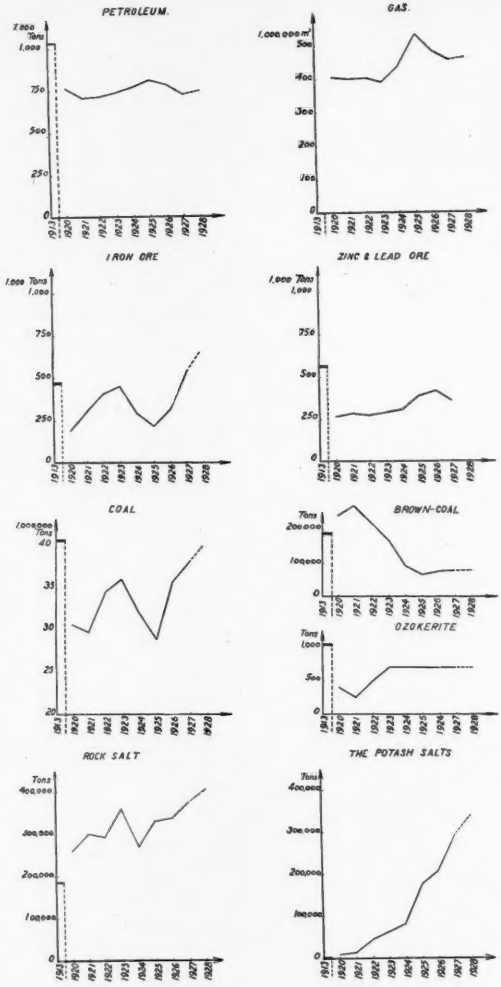


FIG. 1. Diagrams showing mineral production.

The investigations of these associations and institutes are printed in the following publications:

Comptes Rendu of the meetings of the Geological Survey of Poland.
Bulletins of the Geological Survey of Poland.
Annales of the Geological Society of Poland.
Bulletins of the Carpathian Geological Station.
Naphta Industrie.
Journal of Mining and Metallurgy.
Cosmos Publication of the Copernicus Society of the Polish scientists.
Nature and Technique.
Annual Statistical Publications of the Polish Report.

The developments during recent years have been published in: "The Development of the Economic Life in Poland during the Years 1924–1927" (with diagrams), by Kazimierz Bartel, and "The Resources of Mineral Products in Poland," 1927, by Karol Bohdanowicz.

The geological station at Dąbrowa Gornicza is making a geological map of the Polish coal basin on the scale of 1:25000, under the direction of St. Czarnocki.

Cartographic work is in progress on ten geological sheets in various parts of Poland.

The general conditions of mineral production in Poland are illustrated in the diagrams, Fig. 1.

Z. ROZEN.

CRACOW, POLAND.

# REVIEWS

**Limestones, Their Origins, Distribution and Uses.** By F. J. NORTH. Pp. xxiii + 467, figs. 236. Cloth 8vo, Thomas Murby & Co., London, 1930. Price, 16 s.

"This book is essentially a summary of the literature of limestone. . . . It is addressed to those concerned with the winning and utilization of limestone, to the student of geology, of geography, or of economics, and to the general reader desirous of knowing something about the origin of materials of the earth's crust, and of the way in which they have been pressed into the service of man" (Extracted from the Preface). The volume is divided into three parts: (1) The nature, origin and varieties of limestones, (2) The distribution of limestones in the British Isles, and (3) Limestone in relation to scenery, agriculture, water-supply and industry. Five appendices furnish statistical and explanatory material to illustrate the main text. Although the book is limited to the discussion of British limestones, it nevertheless contains a mass of data of interest to those studying limestones in other parts of the world. Perhaps the most interesting feature of the book to readers outside of Great Britain is the characterization of the limestones that have been given local names, as the Hornton stone, the Forest marble, etc. In general the book is well written and excellently illustrated.

W. S. BAYLEY.

**The Study of Crystals.** By T. V. BARKER. Pp. xiv + 137, figs. 181. Cloth 8vo, Thomas Murby & Co., London, 1930. Price, $2.75.

This is a readable account of the properties of crystallized bodies, and an explanation of the causes of their properties, interpreted in the light of modern theories. Practically all the peculiarities of crystals, as distinguished from non-crystalline solids, are described and numerous simple experiments are outlined that illustrate the peculiarities discussed. The meaning and cause of the different axial ratios of different crystallized bodies are logically explained, as are also the properties of isomorphism, isodimorphism and enantiomorphism,—and all in clear language without the use of elaborate mathematical processes. The space-lattice theory of crystallization is briefly discussed and the use of x-rays in the investigation of the structure of the lattice is clearly, though very sketchily, outlined. One of the most valuable parts of the little volume is the

chapter on equilibria between liquid and crystal phases. Simple equilibria diagrams are employed to illustrate the discussion and each is explained in a way that is easily understood. Moreover, under each topic, experiments are suggested which, if carried out successfully, will furnish data that will illustrate the topic and which should yield observation that would be valuable in substantiating the author's generalizations.

The book is an excellent introduction to geometrical, chemical and physical crystallography, because it is so clearly and simply written. It can be understood by anyone who has an elementary knowledge of crystallography, and who wishes to acquaint himself with the modern aspects of the subject, especially from the point of view of theory.

W. S. BAYLEY.

**The Undeveloped Mineral Resources of the South.** By DR. H. M. PAYNE. American Mining Congress, Washington, D. C., 1928.

This book of 368 pages contains a survey of the mineral resources of the thirteen Southern States undertaken for the American Mining Congress. It records in a few brief notes all the known occurrences of mineral substances of possible economic value in the States extending from Virginia to Texas, and briefly describes each. It is a convenient compilation of the knowledge concerning the mineral resources of the south for the use of students, consumers, investors and producers of mineral products.

**Chapters on the Geology of Scotland.** By the late B. N. PEACH and the late JOHN HORNE. Pp. 223, figs. 27, pl. 18. Oxford University Press, London, 1930. (New York, 114 Fifth Ave.) Price, $3.50.

This book brings together much of the valuable life-long work of two masters of Scottish geology. Their previous work has made the region of which they write a classic geological field. Problems of wider significance than the skilful unravelling of complex Scottish geology are raised and discussed. It is an outstanding contribution, and is of particular interest to structural geologists and petrologists. The book contains several colored maps and excellent halftones and is printed in the pleasing style that characterizes all publications of the Oxford Press.

ALAN BATEMAN.

**Outlines of Physical Geology (Pirsson and Schuchert).** By C. R. LONGWELL. Pp. 376, figs. 275. John Wiley & Sons, New York, 1930. Price, $3.00.

A condensation of the Pirsson and Schuchert Text Book of Geology, 3d edition, revised in 1929, by Longwell, Knopf, Bateman, Flint, Agar,

and Dunbar. In this outline, three chapters have been omitted, and all others shortened to yield a briefer and more elementary text desired by some colleges for a short course in general geology.

## BOOKS RECEIVED

**Borate Minerals from the Kramer District, Mohave Desert, California.** By W. T. SCHALLER. Pp. 34, pl. 6, figs. 27. U. S. Geol. Surv. Prof. Paper 158–I, 1930. Borate and associated minerals, origin of deposits. Price, 20 cts.

**The Upper Cretaceous Floras of Alaska,** by A. HOLLICK, with a Description of the Plant-Bearing Beds, by G. C. MARTIN. Pp. 123, pl. 87, figs. 5. U. S. Geol. Surv. Prof. Paper 159, 1930. Price, 80 cts.

**Lithologic Studies of Fine-Grained Upper Cretaceous Sedimentary Rocks, Black Hills Region.** By W. W. RUBEY. Pp. 54, pl. 5, figs. 3: U. S. Geol. Surv. Prof. Paper 165–A, 1930. Chemical and physical features, deposition, occurrence of oil and gas. Price, 25 cts.

**A Flora of Green River Age in the Wind River Basin of Wyoming.** By E. W. BERRY. Pp. 25, pl. 10, figs. 3. U. S. Geol. Surv. Prof. Paper 165–B, 1930. Price, 20 cts.

**Investigations of Mineral Resources and the Mining Industry, 1928.** Canada Dept. of Mines, Mines Br. 710. Ottawa, 1930.

**Investigations in Ore Dressing and Metallurgy, 1928.** Canada Dept of Mines, Mines Br. 711. Ottawa, 1930.

**The New World or Cooke City Mining District, Park County, Montana.** By T. S. LOVERING. Pp. 87, pls. 25, figs. 7. U. S. Geol. Surv. Bull. 811–A, 1929.

**Mineral Industry of Alaska in 1928, and Administrative Report.** By P. S. SMITH. Pp. 96 + xiii, figs. 3. U. S. Geol. Surv. Bull. 813–A, 1930. Selected list of Geological Survey publications on Alaska is appended (13 pp.).

**The Chakachamna-Stony Region, Alaska.** By S. R. CAPPS. Pp. 26, pls. 2. U. S. Geol. Survey Bull. 813–B, 1930.

**Construction and Operation of the Bureau of Mines Experimental Oil-Shale Plant, 1925–1927.** By M. J. GAVIN AND J. S. DESMOND. Pp. 154, figs. 59. U. S. Bur. of Mines Bull. 315, 1930. Price, 70 cts.

**Rock-Strata Gases of the Cripple Creek District, Colo., and Their Effect on Mining.** Pp. 66, figs. 21. U. S. Bur. of Mines Bull. 317, 1930. Price, 20 cts.

**Petroleum Refinery Statistics, 1928.** By C. R. HOPKINS. Pp. 123, figs. 17. U. S. Bur. of Mines Bull. 318, 1930. Price, 25 cts.

**Innovations in Copper Leaching Employing Ferric Sulphate-Sulphuric Acid.** By H. E. KEYES. Pp. 66, figs. 23. U. S. Bur. of Mines Bull. 321, 1930. Price, 20 cts.

**Surface Water Supply of Hawaii, July 1, 1924, to June 30, 1925.** Pp. 155. U. S. Geol. Surv. Water Supply Paper 615, 1930. Price, 20 cts.

**Geology and Water Resources of the Kau District, Hawaii.** By H. T. STEARNS AND W. O. CLARK. Includes a chapter on Ground Water in the Hawaiian Islands, by O. E. Meinzer. Pp. 194, pls. 33, figs. 9. U. S. Geol. Surv. Water Supply Paper 616. Washington, 1930 (Aug.). Price, 85 cts. General and specific occurrences of ground water relating to interesting volcanic areas.

**The Green River and Its Utilization.** By R. R. WOOLLEY. Pp. 456, pls. 35, figs. 29. U. S. Geol. Surv. Water Supply Paper 618, 1930. Price, $1.25.

**Surface Water Supply of the United States, 1926.** *Pt. I.* North Atlantic Slope Drainage Basins. Pp. 274. U. S. Geol. Surv. Water Supply Paper 621, 1930. Price, 30 cts. *Pt. IX.* Colorado River Basin. Pp. 138. U. S. Geol. Surv. Water Supply Paper 629, 1930. Price, 20 cts. *Pt. XI.* Pacific Slope Basins in California. Pp. 419. U. S. Geol. Surv. Water Supply Paper 631, 1930. Price, 65 cts. *Pt. XII–A.* Pacific Slope Basins in Washington and Upper Columbia River Basin. Pp. 154. U. S. Geol. Surv. Water Supply Paper 632, 1930. Price, 20 cts. *Pt. XII–C.* Pacific Slope Basins in Oregon and Lower Columbia River Basin. Pp. 236. U. S. Geol. Surv. Water Supply Paper 634, 1930. Price, 25 cts.

**Results of Air Repressuring and Engineering Study of Williams Pool, Putnam-Moran District, Callahan County, Texas.** By H. B. HILL. Pp. 69, figs. 28. U. S. Bur. of Mines, Tech. Paper 470, 1930. Price, 15 cts.

**Acceleration of Extraction of Soluble Copper from Leached Ores.** By M. GUGGENHEIM AND J. D. SULLIVAN. Pp. 30, figs. 10. U. S. Bur. of Mines Tech. Paper 472, 1930. Price, 10 cts.

**Chemistry of Leaching Chalcocite.** By J. D. SULLIVAN. Pp. 24, figs. 5. U. S. Bur. of Mines Tech. Paper 473, 1930. Price, 10 cts.

**Summarized Data of Silver Production.** By C. W. MERRILL. Pp. 58, figs. 17. U. S. Bur. of Mines, Economic Paper 8, 1930. Price, 20 cts.

**Petroleum Coke. An Economic Survey of its Production and Uses.** Pp. 29, figs. 4. U. S. Bur. of Mines, Economic Paper 9, 1930. Price, 10 cts.

**The Disappearance of the Huronian.** By T. T. QUIRKE AND W. H. COLLINS. Pp. 129, figs. 4, pls. 7, maps 2. Geol. Surv. of Canada, Mem. 160. Ottawa, 1930 (July). Price, 20 cts.

**Lardeau Map-Area, British Columbia.** By J. F. WALKER AND M. F. BANCROFT. Mineral Deposits, by H. C. Gunning. Pp. 142, pls. 8, figs. 7, pocket map. Geol. Surv. of Canada, Mem. 161. Ottawa, 1929 (July, 1930). General geology and detailed discussions and descriptions of silver-lead, gold, and non-metallic deposits.

**Fluorspar Deposits of Canada.** By M. E. WILSON. Pp. 97, pls. 4, figs. 14. Geol. Surv. of Canada, Econ. Geol. Ser. 6. Ottawa, 1929 (July, 1930). Price, 20 cts. General character, origin, and description of deposits according to provinces.

**Peat Bogs in Southeastern Canada.** By V. AUER. Pp. 32, fig. 1, maps 3. Geol. Surv. of Canada, Mem. 162. Ottawa, 1930 (July). Occurrence, growth, origin, of peat.

**Chemismus schweizerischer Gesteine.** By P. NIGGLI, F. DE QUERVAIN, R. U. WINTERHALTER. Pp. 390, figs. 59, map, tables of analyses. Beit. zur Geol. der Schweiz, Geotech. Ser. 14. Bern, 1930. Price, 50 fr.

**L'Activité des Volcans de Boue et Arguments contre la Migration du Pétrole.** By STANISLAS ZUBER. Pp. 47. La Revue Petrolifére, Paris. Price, 15 fr.

**The Mineral Industry during 1929.** Vol. 38. Ed. by G. A. ROUSH. Pp. 845. McGraw-Hill Book Co., New York, 1930.

**Structure of the San Gabriel Mountains North of Los Angeles, California.** By M. L. HILL. Pp. 27, pls. 4, figs. 6, map. Univ. of Calif. Press, Berkeley, 1930. Price, 60 cts.

**Surface Water Supply of the United States, 1926.** Part X. The Great Basin. Pp. 145. U. S. Geol. Surv. Water Supply Paper 630, 1930. Price, 25 cts.

**Geology of the Arkansas Paleozoic Area, with especial reference to oil and gas possibilities.** By CAREY CRONEIS. Pp. 477, pls. 45, figs. 30, structure maps 2. Ark. Geol. Surv. Bull. 3, Little Rock, 1930. Price, $3.20. Describes geology and oil and gas possibilities of Arkansas Paleozoic. Careful detailed descriptions of structures. Well logs and statistics. Thorough.

**Estudos Geologicos na Chapada Diamantina, Bahia.** By H. E. WILLIAMS. Pp. 16, illustrated. Serv. Geol. e Min. do Brasil, Bol. 44, Rio de Janeiro, 1930. Regional geology; occurrence, origin, and character of diamonds.

**Provincia Magmatica de Roroimã, Brasil Septent.** By D. GUIMARAES. Pp. 57, illustrated. Serv. Geol. e Min. do Brasil, Bol. 45, Rio de Janeiro, 1930. A petrologic study of this basic magmatic province in northwestern Brazil.

**A Geologia do Petroleo no Estado de S. Paulo.** By L. F. M. REGO. Pp. 110, figs. 24. Serv. Geol. e Min. do Brasil, Bull. 46, Rio de Janeiro, 1930 (Sept.). Stratigraphy; structure; petroleum occurrences, character and origin.

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Copies of books mentioned under "Reviews" or under our "New Book List" (see advertisement page) may be purchased through our Journal Bookshop by writing to W. S. Bayley, University of Illinois, Urbana, Ill.

# SOCIETY OF ECONOMIC GEOLOGISTS

The eleventh annual meeting of the Society of Economic Geologists will be held in Toronto, Canada, on December 29th to 31st, 1930, as guests of the University of Toronto. The Society will meet with the Geological Society of America and affiliated societies, the program being arranged so as to eliminate conflict in every way possible. Joint meetings will be arranged where feasible. During the period of the meetings an informal luncheon will be held for members of the Society.

E. S. Moore is chairman of a committee on arrangements for the meetings.

The Program Committee consists of J. T. Singewald, Jr., chairman (Johns Hopkins University, Baltimore, Md.), B. S. Butler, E. S. Bastin, H. G. Ferguson, and E. S. Moore.

Papers from any member may be submitted to the Program Committee, and for members outside of North America, accepted papers may in some cases be read or presented in abstract by another member familiar with the contents, or they may be read by title. Papers appearing on the program may, if the author wishes, be submitted for the decision of the Publications Committee, whether or not they be read in full at the meeting.

# SCIENTIFIC NOTES AND NEWS

Alexander McDonald is now chief geologist of the North Butte Mining Co., Butte, Montana.

Robert E. Landon, recently with the Anaconda Copper Mining Company, has joined the staff of the U. S. Geological Survey.

W. H. Collins, Director of the Canada Geological Survey, recently spent two months in field work in Sudbury, Ontario.

David B. Reger, who lately resigned as associate geologist of the West Virginia Geological Survey, has opened an office as consulting geologist at 217 High Street, Morgantown, W. Va.

R. Murray-Hughes has returned to England after a trip to Jugoslavia.

E. L. Bruce, research professor of the Department of Geology, Queen's University, Kingston, Canada, has returned after a summer in Finland.

Ralph Tuck, of Cornell University, has joined the staff of the Geology Department of the University of Cincinnati as assistant professor.

H. Ries, professor of economic geology, Cornell University, has returned from a trip to the Hawaiian Islands.

A. L. Du Toit, consulting geologist to DeBeers Consolidated Mines and associate editor of this journal, has received from the South African Association for the Advancement of Science the gold medal and grant for 1930, awarded to the scientist who is considered to have done the most important scientific and research work during the year.

W. H. Newhouse, associate professor of economic geology, Massachusetts Institute of Technology, spent the summer in western mining camps investigating structural relations of ore shoots, under a grant received from the Institute.

P. H. Price, formerly of Cornell University, is now Assistant State Geologist of the West Virginia Geological Survey.

John W. Finch has been made Dean of the School of Mines at the University of Idaho, Moscow, Idaho.

A. A. Wedel, of Cornell University, has joined the staff of the Pure Oil Company.

Austin Gudmundsen, after a year at the Carnegie Institute of Technology, Pittsburgh, Pa., in fuel research work, has returned to his professorship in the University of Utah.

R. H. Clarke is engaged in geophysical prospecting work in Russia for the Radiore Company.

A. W. Hahn, of Salt Lake City, Utah, lately returned from five months spent in Russia, Germany, and England.

Julius Kruttschnitt, who for eighteen years has been with the American Smelting and Refining Co., is now manager of operations at Mount Isa, Queensland, Australia.

Stanley R. Moore, formerly located at Wallace, Idaho, is in charge of operations at the Standard Silver-Lead Mining Co., Helena, Mont.

Alfred James will sail for South Africa from London in October, for a stay of three years.

H. H. Ray, who has been for three years in the Philippines, as general superintendent for Benguet Consolidated, is now at Los Gatos, Calif.

It was stated on page 426 of the June issue that the late Dr. Percy A. Wagner placed on record the discovery of stichtite at the Amianthus Mine, Transvaal. It was, however, Dr. A. L. Hall who first recorded this occurrence, in 1921.

At the Vulture mining property, near Wickenburg, Arizona, a lost or faulted portion of the vein has been discovered as a result of extensive geological and exploration work.

A high-grade deposit of bornite and chalcopyrite is reported to have been found by the Northern Aerial Mineral Exploration Company in the Coppermine River area of northwestern Canada.

Ward's extensive museum of mineral specimens, at Rochester, N. Y., said to be the most complete exhibit in the country, was recently burned.

The Society of Economic Paleontologists and Mineralogists held its annual fall meeting on October 25 at Ardmore, Okla. Under the direction of C. E. Decker, opportunities were given to study and collect Pennsylvanian fossils near the Arbuckle Mountains.

The 26th Annual New England Intercollegiate Geological Excursion was held Oct. 10 and 11, covering parts of the northern Connecticut Triassic Basin, radiating from Amherst.

The 16th session of the International Geological Congress will be held in the United States in early June, 1932. The first circular of the Organizing Committee has just been issued, of which an abstract follows. Those interested may obtain further details and circulars from W. C. Mendenhall, General Secretary, 16th International Congress, Washington, D. C.

Any interested person may register; places on excursions will be especially reserved for geologists, mining engineers and geographers.

The usual special monograph will be "The Petroleum Resources of the World." Other suggested topics are: (1) Geologic Time; (2) Batholiths and Related Intrusives; (3) Origin of the Mississippi and Silesia Type of Lead-Zinc Deposits; (4) Zonal Relations of Metalliferous Deposits; (5) Cycles in Sedimentation; (6) Major Divisions of the Paleozoic; (7)

Boundaries and Major Divisions of the Tertiary; (8) Adaptation of Extinct Animals and Plants to Environment; (9) Physiographic Processes and Results in Arid Regions; (10) Fossil Man.

Excursions will take place before, during, and after the Congress. The main pre-Congress excursions will start from New York or Washington in late May and will occupy about ten days. The following are tentatively considered: (1) Adirondack Mts. and Connecticut (bus),—petrology, structure, geomorphology; (2) Mining districts of the Eastern States and Mississippi Valley (rail)—economic geology; (3) Appalachian Mts. of the Virginias and Tennessee (bus),—structure, stratigraphy; (4) Western New York and Pennsylvania (bus),—stratigraphy, structure, glaciology, physiography; (5) Atlantic Coastal Plain (boat and bus)—Tertiary and Cretaceous; (6) Glacial geology of North-Central States; (7) San Francisco to New York (rail)—stratigraphy, economic, glacial; (8) various short excursions from New York.

Excursions during the Congress will be short ones to nearby parts of Pennsylvania, Maryland and Virginia.

The post-Congress excursions are: (1) First Transcontinental (special train), via New Mexico, Arizona, and California, returning via Wyoming (Yellowstone), Utah and Colorado (32 days)—metal mines, petroleum, general geology, scenic features. (2) Second Transcontinental (rail), Central Arizona, California, returning via Oregon, Washington, Idaho, Montana, North Dakota, Michigan iron ranges, Niagara (33 days)—scenic features, general geology, mining geology. (3) Lake Superior iron and copper districts (rail and bus)—economic geology, glaciation, pre-Cambrian (13 days). (4) Oklahoma and Texas—petroleum and stratigraphy (10 days).

Excursions will also be run to Alaska and Hawaii if enough desire them. Definite costs will be announced later. In general, the total cost for rail trips will be about $15 per day and for bus trips about $10 per day.

Those interested are asked to express excursion preferences. This involves no obligation, but is merely to guide the Committee.

Frank James Katz, in charge of the Division of Mineral Resources and Statistics, U. S. Bureau of Mines, died suddenly of a heart attack on August 21, at Washington.

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The recently published 20-volume index (336 pages) of ECONOMIC GEOLOGY for 1905 to 1925, compiled by J. M. Nickles, may be obtained for $3.00 from W. S. Bayley, University of Illinois, Urbana, Ill.

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